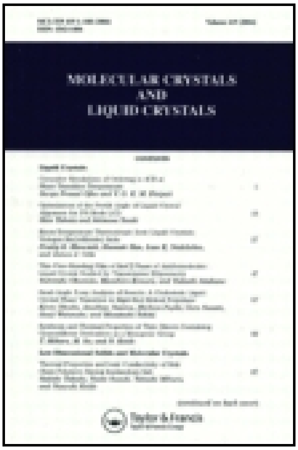

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Phase Separation of Liquid Crystals in Polymers

John L. West [a]

[a] Liquid Crystal Institute, Ken State University, Kent, OH, 44242, U.S.A.

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PHASE SEPARATION OF LIQUID CRYSTALS IN POLYMERS

JOHN L. WEST
Liquid Crystal Institute, Kent State University, Kent, OH 44242, U.S.A.

Abstract New optoelectronic materials based on polymer dispersed liquid crystals (PDLC) show great potential for application in displays, temperature sensors, optical computing and for solar energy control. We report liquid crystal, thermoset or thermoplastic materials. PDLC materials may be formed by several different processes. The liquid crystal may be dissolved in low molecular weight polymer precursors, in a thermoplastic melt or with a thermoplastic in a common solvent. Subsequent polymerization, cooling of the polymer melt or solvent evaporation lead to liquid crystal immiscibility, droplet formation and growth, and polymer gelation. The optoelectronic properties of these materials are affected by the droplet morphology. Specific examples are presented for each of these processes and it is demonstrated how the droplet morphology and density, and thus device performance, can be controlled by each method. The thermoplastics are suitable for forming films by a variety of techniques. A range of polymers and liquid crystals may be used to form PDLC materials, allowing them to be tailored for any of a number of applications.

INTRODUCTION

Polymer dispersed liquid crystals (PDLCs) have recently been reported.[1] These materials are formed by the incorporation of liquid crystals in a crosslinked epoxy binder or in a UV cured polymer matrix.[2,3] The materials may be switched from a scattering to a clear state by application of an electric field. These materials show great promise in a variety of display applications, optical computing, optical hardening, and light valves.

Light is scattered from films of liquid crystal droplets dispersed in a binder because of a mismatch of the refractive index of the droplet and the polymer binder.[1,4] The director of the liquid crystal within the droplets has no preferred orientation but varies randomly from droplet to droplet in the absence of an electric field. The liquid crystal has a positive dielectric anisotropy and therefore aligns parallel to an electric field. Figure 1 shows a schematic of these films in the field *OFF* and field *ON* states. Light is efficiently scattered in the field *OFF* state because of the mismatch of the refractive index of the droplets and the polymer binder. However, in the field *ON* state the alignment of the liquid crystal results in the droplets having an effective refractive index equal to the ordinary refractive index of the liquid crystal, n_0, for light incident normal to the film. The polymer binder has a refractive index, n_p, essentially equal to n_0 and therefore the film is transparent.[1]

PDLC materials are also formed using thermoplastics which offer a great variety of usable polymers, methods of forming the PDLC materials, and techniques of forming films. The formation of the thermoplastic PDLC materials may be achieved by three basic methods: the liquid crystal is dissolved in the prepolymer followed by polymerization (polymerization induced phase separation, PIPS); the liquid crystal is dissolved in the polymer melt followed by cooling (thermally induced phase separation, TIPS); or the liquid crystal is dissolved with the polymer in a common solvent followed by evaporation of the solvent (solvent induced phase separation, SIPS). Each of these methods results in droplets of the liquid crystal incorporated in the polymer binder. This paper will report specific examples of each method, means of controlling droplet size and density, the optoelectronic

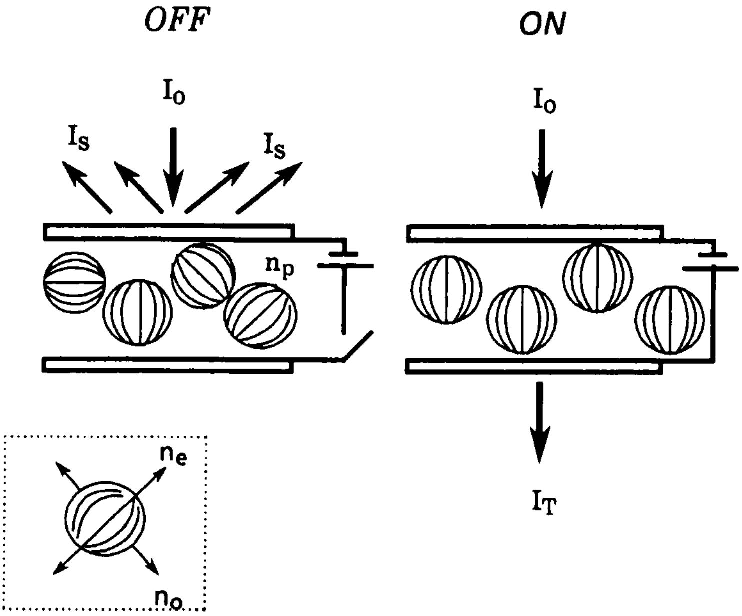

FIGURE 1

Illustration of the principle of optoelectronic operation of the PDLC films. I_0 = Incident light, I_S = scattered light, I_T = transmitted light, n_e = extraordinary refractive index, n_o = ordinary refractive index, n_p = polymer refractive index.

properties of the materials, and means of processing the material into films.

EXPERIMENTAL

PIPS

A thermoset epoxy was formed by mixing Epon 828, Capcure 3-800 (Miller Stephenson Company), and the eutectic liquid crystal mixture E7 (EM Chemicals) in a 1:1:1 ratio by weight. A second thermoset epoxy was formed by mixing by weight 20% MK-107 (Wilmington Chemical Co), 11% Epon 828, 28% Capcure 3-800, and 41% E7. Epon 828 is the reaction product of epichlorohydrin and bisphenol A; Capcure 3-800 is a trifunctional mercaptan terminated liquid polymer. MK-107 is the trade name for cyclohexanedimethanol diglycidyl ether, and E7 is an eutectic mixture of cyanobiphenyls and triphenyls. The resulting solutions are thoroughly mixed and poured with 26 μm Alufrit spacers between transparent, conducting glass electrodes and squeezed to form uniform 26 μm thick films. The films are cured between room temperature and 100°C. An electric field is placed across the films by applying a voltage to the electrodes of the substrate.

A thermoplastic epoxy was formed by mixing one equivalent of Epon 828 with one equivalent of hexylamine. The mixture was thoroughly stirred and the eutectic liquid crystal mixture E7 was added to form a 33% by weight solution. The mixture was cured in bulk in a sealed vial at 65°C overnight. The resulting plastic is hard and milky white at room temperature. The material is a clear viscous liquid when heated to 100°C. Alufrit spacers of 26 μm are used to form a uniform film of the material between glass with transparent, conducting electrodes. The glass sandwiched film is cooled to room temperature. An electric field is placed across the film by applying a voltage to the electrodes of the glass substrate.

TIPS

A thermoplastic epoxy was formed by mixing one equivalent of Epon 828 with one equivalent of t-butyl amine. The mixture was thoroughly stirred and cured in bulk in a sealed vial at 65°C overnight. The resulting epoxy is a clear, glassy solid at room temperature and a highly viscous liquid at 100°C. E7 was added to the polymer melt to form a 33% by weight homogeneous solution. The material was placed between transparent, conducting glass with 26 μm spacers and cooled to room temperature. An electric field is placed across the film by applying a voltage to the electrodes of the glass substrate.

SIPS

A 6.3% E7 and 4.2% by weight solution of polymethylmethacrylate in chloroform is made by stirring the components in the solvent for one hour at room temperature. The resulting solution is clear and homogeneous. The solution was coated on a substrate of transparent, conducting glass by doctor blading or dip coating. The solvent was evaporated in a clean environment. A second conducting glass substrate was adhered to the film with pressure and heat. An electric field was placed across the film by applying a voltage to the electrodes of the glass substrate.

RESULTS AND DISCUSSION

Phase separation of the homogeneous solution of liquid crystal and polymer results during setting for each of the three phase separation processes. This leads to formation of droplets of liquid crystals dispersed in the polymer binder forming a scattering film. PIPS may be depicted on a time line (Figure 2). The liquid crystal is soluble in the low-molecular weight epon resin and cure agent. Polymerization results in a change of the chemical potential of the polymer solvent and at some point phase separation of the liquid crystal results, leading to droplet nucleation and growth. The liquid crystal continues to phase separate until gelation of the polymer halts the droplet growth. The material appears white at this stage due to light scattered by

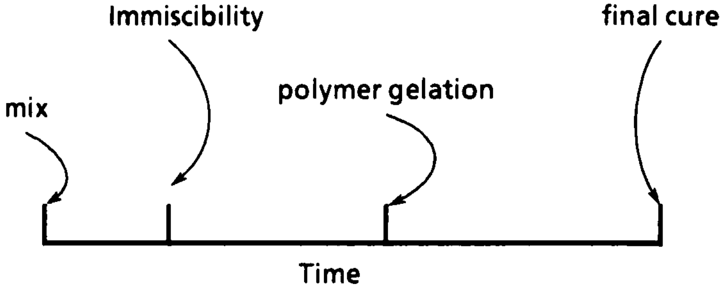

FIGURE 2

Schematic representation of the PIPS process.

the liquid crystal droplets. The polymerization process continues and the liquid crystal within the droplets is purified. Purification of the liquid crystal within the droplets results in an increase in the nematic-to-isotropic phase transition temperature. The refractive index of the liquid crystal in its isotropic phase is more closely matched with the polymer than in the randomly oriented nematic phase. Thus, the film shows a large decrease in the intensity of scattered light at the nematic to isotropic phase transition offering an excellent means of monitoring this transition. The purification of the liquid crystal within the droplets may be due to slow transfer of lower molecular weight oligomers dissolved in the liquid crystal to the polymer binder where they react, lengthening the epoxy chains. The nematic-to-isotropic phase transition becomes narrower and approaches the temperature of the bulk liquid crystal as the polymerization continues, indicating that the composition of the liquid crystal within the droplets is essentially the same as that of the bulk.

The droplet size and density for materials formed by the PIPS process are highly dependent on the cure temperature. Figure 3

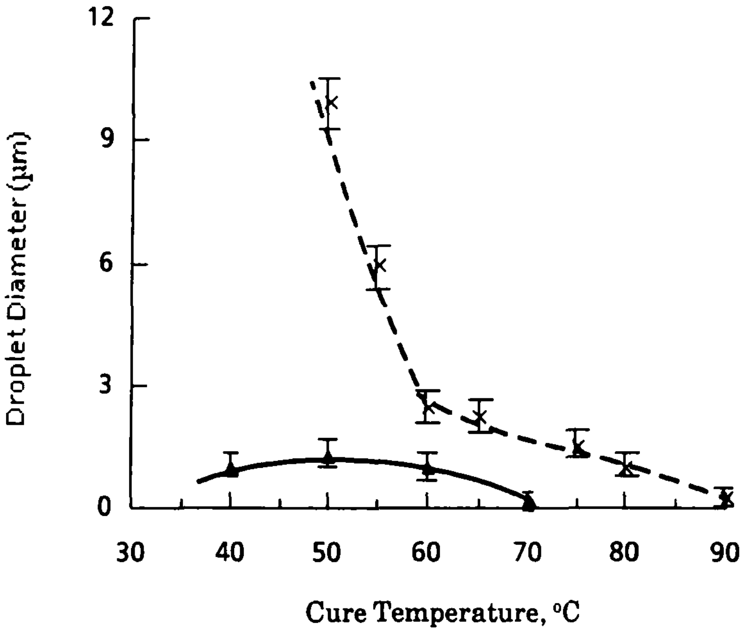

FIGURE 3

Graph of average droplet diameter as a function of cure temperature for: —— 1:1:1 mixture of epon 828, capcure 3800 and E7: – – – 20%MK-107, 11% epon 828, 28% capcure 3-800 and 41%E7.

gives the average droplet size as a function of cure temperature for PDLC films formed from 1:1:1 Epon 828, Capcure 3-800, and E7 or from 20% MK-107, 11% Epon 828, 28% Capcure 3-800, and 41% E7. The droplet size is a complex function of the cure temperature showing a maximum in droplet size at a cure temperature of about 50°C for the 1:1:1 film and decreasing regularly for films made with the MK-107. This is similar to the phenomena found for rubber modified epoxies.[5] Several competing factors of the curing process affect the droplet size: viscosity of the polymer, rate of diffusion of the liquid crystal, solubility of the liquid crystal in the polymer, types of materials used, and the rate of polymerization. Each of these is affected differently by the cure temperature with the result that the droplet size varies in a complex manner with cure temperature.

Epon 828 cured with Capcure 3-800 results in a crosslinked, thermoset polymer. Epon 828 cured with a difunctional cure agent, such as hexlyamine or *t*-butylamine, results in a noncrosslinked thermoplastic. The liquid crystal may be mixed with the epon and difunctional cure agent followed by polymerization. Phase separation of the liquid crystal will occur during polymerization, completely analogous to the thermoset epoxies. However, the resulting material may be melted. The PDLC material resulting from mixing Epon 828, hexlyamine, and E7 is a liquid at 100°C. This allows displays to be made simply by heating the PDLC material while squeezing between substrate electrodes. The resulting light shutter may be reworked by heating above the melting point of the PDLC material.

TIPS results when cooling a liquid crystal/thermoplastic melt. The liquid crystal is soluble in the polymer melt. This is clearly shown by dissolving the liquid crystal in the melt of the polymer formed by reaction of Epon 828 and *t*-butylamine. The *t*-

butylamine was used to cure the epon because of the low melt temperature of the resulting polymer, <100°C. Cooling of the mixture results in phase separation, droplet formation and growth, and polymer gelation. Figure 4 is the phase diagram of E7 in the *t*-butylamine cured Epon. The phase separation temperature was determined as the temperature at which an increase in the light scattered by the material occurred. The intensity of the scattered light was monitored as a decrease in the light transmitted through the material. Figure 5 shows the intensity of light transmitted through samples of various composition as a function of temperature. The polymer is the continuous phase even for relatively high E7 concentrations. Only for E7 concentrations greater than 80% is a continuous liquid crystal phase observed. The polymer has a finite solubility in the liquid crystal and is observed as a depression in the nematic-to-isotropic phase transition temperature for high E7 concentrations.

The rate of cooling of the polymer melt affects the resulting droplet morphology. Figure 6 is a plot of the average droplet diameter *vs* the rate of cooling. Rapid cooling results in smaller droplets and more liquid crystal remaining in the binder. Slower cooling results in larger droplets. This is because slower cooling allows more time for phase separation, droplet growth, and droplet coalescence. The droplet size and density has a major influence on the optoelectronic response of these materials and on the scattering efficiency of these films.[6,7] The scattering efficiency of the PDLC films is maximized when the droplet size is on the order of the wavelength of light. The driving voltage increases and the turn off time decreases with decreasing droplet diameter. Therefore, the cooling rate of thermoplastic PDLC materials offers an excellent means of controlling device performance.

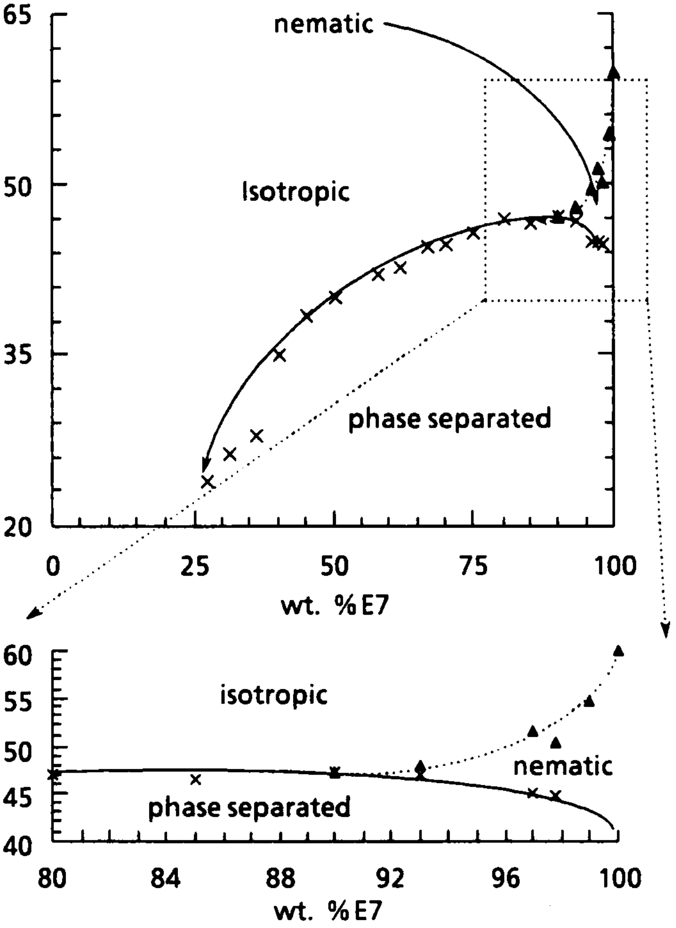

FIGURE 4

Phase diagram of E7 and t-butylamine cured epon 828:
——— = droplet formation, ···· = nematic-isotropic transition.

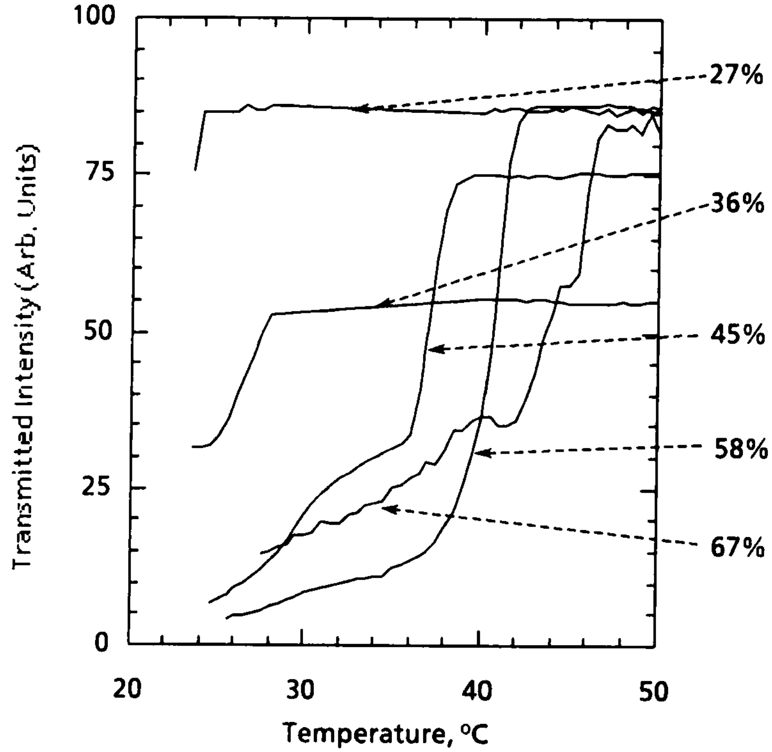

FIGURE 5

Relative transmission *vs* temperature for films of varying liquid crystal composition in a *t*-butylamine cured Epon 828.

SIPS results when the solvent is removed from a liquid crystal and thermoplastic solution dissolved in a common solvent. Figure 7 is a ternary phase diagram showing schematically the SIPS process. A system consisting of polymer, liquid crystal, and a common solvent of composition represented by point X is made. Evaporation of the solvent moves the system

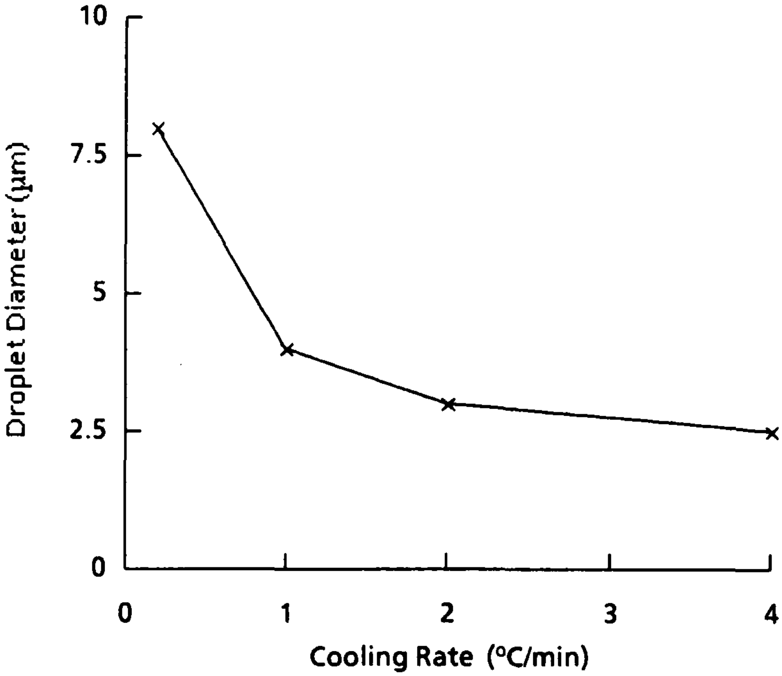

Figure 6

Droplet diameter *vs* the rate of cooling of a thermoplastic melt consisting of E7 dissolved in Epon 828 cured with *t*-butylamine.

along the line XA. Upon crossing the miscibility gap droplets will form and grow until gelation of the polymer. Point A represents the final composition of the SIPS formed PDLC film. E7 and polymethylmethacrylate (PMMA), dissolved in chloroform were used to form PDLC films by the SIPS process. Evaporation of the chloroform results in the system crossing the miscibility gap, leading to droplet formation and growth and polymer gelation. The droplet size and density are controlled by

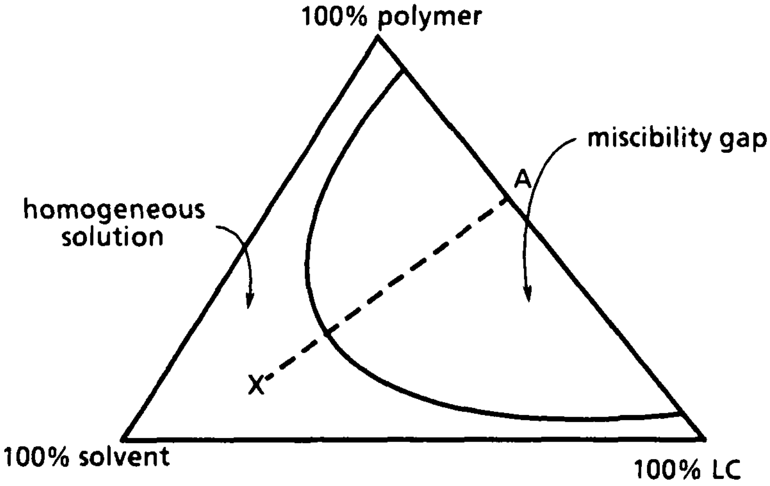

FIGURE 7

Schematic ternary phase diagram of the SIPS process.

the rate of solvent removal. The rate of solvent removal is controlled by the rate at which air is passed over the sample; the faster the air flow rate, the faster the rate of evaporation. Table 1 lists the time to droplet formation and the droplet size as a function of the air flow rate; the slower the air flow rate, and thus the rate of solvent evaporation, the larger the droplet size.

FILM FORMING TECHNIQUES

Thermoplastic PDLC materials may be formed into films by a variety of standard film forming techniques. Solvent coating techniques such as dip coating, doctor blading and wire-wound

Table 1. Droplet Size and Formation Time

Air Flow Rate (ml/min)	Time to Droplet Formation (min)	Droplet Size (um)
100	34	⩽1
20	150	3
3	720	12

rods have been used to form uniform films on plastic substrates. Hot melt techniques may also be used with thermoplastic films not containing solvent. The resulting films may be laminated using heat and pressure to form a PDLC film sandwiched between conducting plastic substrates. Draw-down coaters may be used to form films of thermoset PDLC materials. Large area films are possible as are continuous film-forming processes commonly used in plastic film manufacture.

CONCLUSION

PDLC materials are suitable for a variety of applications ranging from large area displays to solar control windows. The materials used are commercially available in large quantities and may be processed by standard film-forming techniques, making the PDLC devices easy and inexpensive to manufacture. They have great commercial potential as optoelectronic displays, thermal indicators and solar control devices.

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