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Polymer Dispersed Liquid Crystals: A Look Back, A Look Ahead Paul S. Drzaic – Raychem Corporation

t's been a little over 10 years since serious effort began on the development of polymer dispersed liquid crystal (PDLC or NCAP) technology. Since that time, remarkable advances have been made in crafting materials that are useful in several different areas of application. Equally remarkable is that the technological interest in these materials has sparked renewed interest in the scientific investigation of liquid crystals confined to small cavities. As is usual in these types of endeavours, the technological and scientific aspects of this work have enriched each other and led to new inventions and discoveries.

This article highlights some of the recent aspects of PDLC science and technology. In a short space it is not possible to do more than touch briefly on more than a few areas, or to properly cite the many sources of work in this area. Rather, the intent is to give an idea of the scope of present work in the area of PDLCs, as well as to point to some directions likely in future work.

Recipes

Two major routes have become established as means of creating polymer dispersed liquid crystal materials. One scheme involves the emulsification of a liquid crystal in an aqueous solution of a film-forming polymer (like poly(vinyl alcohol)). The second route uses phase separation to create a PDLC film from a homogenous single-phase solution of liquid crystal and polymer. Acrylate photopolymerization has proven to be the most popular chemistry for formation of PDLC devices using the phase separation route, with epoxy chemistry also finding much usage.

A range of polymer morphologies can be found in PDLC devices, varying primarily in the size and distribution of nematic droplets, as well as the extent of interconnection with neighbouring domains. Figure 1 shows electron micrographs of two PDLC films, one with relatively discrete droplets and the other with highly interconnected nematic domains. Both emulsion and phase separation films can show a range of morphologies, depending on the nature of the polymer, the liquid crystal concentration





Figure 1 Electron micrographs of PDLC films with different morphologies. The liquid crystal has been removed for the photographs, exposing the polymer network. The polymer content in each film is approximately 20%. (Top) Cross section (side) view of film created by emulsifying a liquid crystal into an aqueous solution of poly(vinyl alcohol). (Bottom) Top view of film created by photo-induced phase separation of a UV-curable polymer.

The top photograph courtesy of Marc Rouberol and John West of Kent State University.

and the processing conditions. In phase separation processes the polymer morphology can also be impacted by the phase separation route the system chooses. Nucleation and growth processes tend to give discrete droplet structures, while spinodal decomposition usually leads to more interconnected structures. Despite these apparent differences, the basic electro-optical properties of PDLC films are typically the same whether they are formed by either emulsification or by phase separation, or whether the droplets are discrete or interconnected.

In the last several years a number of other matrix materials have been demonstrated as useful in creating dispersed liquid crystal structures. For example, inorganic matrices can be created by sol-gel chemistry or by mixing liquid crystals with silica sols. Reactive liquid crystals (mesogenic diacrylates) have also been used to create some interesting network structures within a liquid crystal film. In these systems the liquid crystalline monomers adopt the alignment of the surrounding liquid crystal before reaction. After photopolymerization they form a highly crosslinked structure which maintains the alignment properties of the liquid crystal at the time of polymerization. As such, these networks can stabilize different textures or alignment states of the liquid crystal.

Liquid Crystals in Cavities

Interest in the structure of nematic droplets actually predates the introduction of PDLC devices by at least a decade or two. A veritable zoo of different droplet structures has been observed in solution: bipolar, twisted bipolar, concentric, radial, twisted radial, and equatorial droplets are a few examples (Figure 2). In cholesteric droplets more complex textures can be found. The structures found in PDLC films depend on the anchoring strength of the liquid crystal at the droplet surface, the size and shape of the cavity, and the elastic properties of the liquid crystal.

The large surface area and curved surfaces found in small nematic droplets has led to examination of so-called surface elastic constants which are normally ignored in parallel-plane devices. In particular, the K_{24} (saddle-splay) elastic constant has been predicted by theory to influence the stability of different droplet configurations. Along experimental lines, the first measurement of the K_{24} constant has recently been reported for a liquid crystal in a confined structure (although the structure was a narrow-bore cylinder, not a droplet).

Electro-optical Effects

A "standard" PDLC device possesses a scattering zero-field state and transparent high-field state. Early efforts in PDLC's focused on understanding and optimizing the characteristics of devices made from these materials. These efforts have been quite successful; the reorientation fields for PDLC devices have been reduced from around 5V/ μ m (common in early films) to as low as 0.5 V/ μ m. For a 10 μ m thick device this leads to an operating voltage of 5V, making today's PDLC's compatible with semiconductor drive technology.

While the reorientation field of a PDLC material depends on the liquid crystal properties and domain size, the choice of



Figure 2 Schematic of some different director fields which have been observed in nematic droplets. Parallel wall alignment: a) Bipolar; b) Twisted bipolar; c) Concentric: perpendicular wall alignment; d) Radial; e) Twisted radial; f) Equatorial.

polymer is far more important. It is probable that the anchoring energy of the liquid crystal at the droplet surface dominates the reorientation field required for the film. It is usually not possible today to predict the reorientation field for a given combination of liquid crystal and polymer, as these anchoring interactions are for the most part poorly characterized and understood.

There have been several refinements in the understanding of light scattering properties in PDLC films. In films at low field each nematic domain possesses a random orientation with respect to its neighbours. Light passing through a film will see a rapid change in refractive index as it travels from droplet to droplet (Figure 3). This change in the refractive index between neighbouring droplets leads to the intense light scattering observed in PDLC films. At high fields, each domain is aligned in a common direction, which removes the refractive index difference between neighbours. Since the refractive index of the film no longer varies



Figure 3 Idealized scheme for a collection of bipolar droplets at low and high fields. At low fields, the randomized orientation of the bipolar director field lead to rapid variations of the refractive index within the film. These rapid changes in index leads to strong light scattering. At high fields, the common orientation of the director fields provides a more uniform refractive index throughout the film. Scattering is weak, and the film appears transparent.

rapidly in space, light scattering is reduced. While the difference in refractive index between the liquid crystal and polymer can also lead to light scattering, this effect tends to be much weaker than the dropletdroplet scattering, particularly at low concentrations of polymer.

Some interesting variations in PDLC properties have been achieved by dispersing different liquid crystalline phases in polymers. In many cases the electro-optical effects are similar to those found in parallel plate cell geometries without a polymer matrix. For example, in chiral smectic C* materials both bistable switching and deformed helix modes have been demonstrated. Electroclinic effects in chiral smectic A* materials have been observed, as well as the formation of stable smectic A homeotropic and focal conic textures. Focal conic, planar, and homeotropic states have



Figure 4 A reflective NCAP (PDLC) display used as a control panel on Xerox model 4850 and 4890 copiers. The display consists of a dichroic PDLC panel coupled to colour reflectors. The display exhibits high relative brightness under both high and low illumination conditions, and possesses excellent viewing angle without backlighting.

also been observed in dispersed cholesteric materials, which can be used to create either monostable or bistable display devices. Reverse mode devices (transparent at low fields, scattering at high fields) can be created by several different routes.

Novel film structures can be created through processing variations. For example, holographic PDLC films have been formed by inducing photopolymerized phase separation by intersecting laser beams. Such films show periodic variations in droplet size or density, and exhibit diffraction effects which can be controlled by varying the droplet alignment with an electric field.

Applications

The first applications of PDLC devices were as large area shutters for architectural windows. The switchable scattering states of the film are useful in privacy and shading applications within buildings. More recently, PDLC films containing dichroic dyes have been growing in popularity for control panel applications. Dichroic PDLC films switch between dark and light states through the reorientation of dye molecules within the droplet, and can be used to form attractive control panel devices. Figure 4 shows an example of such a device.

PDLC films are natural in applications where light efficiency is important. Since PDLC scattering effects do not require the use of polarizers, devices based on PDLC films can be two to three times brighter than corresponding polarizer-based displays. A particularly attractive application along these lines is in projection liquid crystal displays. A PDLC film coupled to an active matrix substrate makes a highefficiency light valve; three such panels, can be used to make a full-colour (RGB) projector. It is likely that PDLC-based projectors will appear on the market within the next year.

The Future

The demands of applications will force future improvements in conventional PDLC devices. It is likely that films with even lower operating voltages, faster response times, and better optical properties can be developed. In many cases it is not possible to predict the "ultimate" electro-optical properties since the physics of many aspects of PDLC devices (like the operating voltage) are still poorly understood.

One of the exciting aspects of PDLC materials is that the rate of discovery and invention continues at a rapid pace. Polymers have been liberated from the surface of liquid crystal cells by PDLC devices, and allowed to share the volume of the liquid crystal cell. The sheer number of variations possible on this theme guarantee an interesting ride for some time to come.

Paul Drzaic is a Principal Scientist at Raychem Corporation, where he is involved in the development of display devices based on polymer dispersed liquid crystals. He is author of a book, *Liquid Crystal Dispersions*, which will be published this Spring by World Scientific.

Letter to the Editor...

Dear Editor

One of the most outstanding conferences on liquid crystals was held this summer in marvellous Budapest. The organizers did their best to provide the successful scientific work and the pleasant rest time during the Conference. Nevertheless, the incredible number of presentations made the work in the Conference Palace rather hard. Simultaneous presentation in three sections provoked a strong desire to split ourselves into three pieces, while poster sessions gave the only opportunity to read the titles and look through the abstracts during the few hours of the poster presentation. Such a big conference is undoubtedly needed as it allows participants to meet with specialists of all fields of liquid crystal science. At the same time we think that some reasonable changes might be made in the form of its organization. ILCC, indeed, has to remain the biggest conference of liquid crystals but we'd like to propose a sufficient reduction of the quantity of reports. Our common opinion is that only oral presentations might be contributed to ILCC. These reports should be collected by the Program Committee on the basis of those presented at smaller topical conferences and workshops. So, ILCC becomes the conference of a limited quantity of excellent reports for the great number of participants.

We believe that such alteration will make ILCC more effective, and we would be glad to invite readers of Liquid Crystals Today to join this discussion.

Audrey Iljin, Victor Reshetnyak, Yuriy Reznikov. Institute of Physics, Kiev.

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