Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Glass dispersed liquid crystals

J. M. Oton[a]; A. Serrano[a]; C. J. Serna[b]; D. Levy[b]
[a] Departamento Tecnología Fotónica, ETSI Telecomunicación, Ciudad Universitaria, Madrid, Spain [b] Instituto de Ciencia de Materiales, CSIC, Madrid, Spain

To cite this Article Oton, J. M. , Serrano, A. , Serna, C. J. and Levy, D.(1991) 'Glass dispersed liquid crystals', Liquid Crystals, 10: 5, 733 — 739

To link to this Article: DOI: 10.1080/02678299108241741

URL: http://dx.doi.org/10.1080/02678299108241741

LIQUID CRYSTALS, 1991, VOL. 10, NO. 5, 733–739

PRELIMINARY COMMUNICATION

Glass dispersed liquid crystals

by J. M. OTÓN*†, A. SERRANO†, C. J. SERNA‡ and D. LEVY‡

† Departamento Tecnología Fotónica, ETSI Telecomunicación,
Ciudad Universitaria, 28040 Madrid, Spain
‡ Instituto de Ciencia de Materiales, CSIC, Serrano 115 dpdo.,
28006 Madrid, Spain

(*Received 1 May 1991; accepted 20 June 1991*)

Sol–gel processes have been used to trap liquid crystal droplets into silica gel glasses. Several monomer mixtures and liquid crystals have been used. In most cases, trapping of spherical droplets has been achieved and droplet sizes from < 1 to 200 μm have been obtained. Switching between opaque and transparent states has been successfully tested; the voltages required for switching and the electrooptical response times are related to pore surface composition. These voltages and times are similar to those found in polymer dispersed spherical droplets.

Polymer dispersed liquid crystals (PDLC) have been widely used in commercial electrooptic devices since the pioneering work of Fergason [1]. Improvements of original materials, response time and droplet uniformity and shape have led to applications well beyond transparent/opaque displays to include spatial light modulators, colour displays, optical shutters, light valves and projection screens [2–4]. On the other hand, the recently applied sol–gel process [5] has been successfully used for the manufacture of silica glasses. In general, a sol–gel process begins with the formation of a colloidal suspension of the reaction products called a sol, usually from metal alkoxide monomers through hydrolysis and polycondensation reactions, at room temperature. The sol undergoes a transition to a soft porous wet gel, which eventually becomes a solid porous aggregate of extremely small particles known as a xerogel. Using organo-silicon compounds under certain reaction conditions, the xerogel may eventually become a porous transparent silica glass. Glasses containing organic dyes or photochromic molecules [6–8] have recently been prepared. Gel–glass matrices may show excellent optical properties; indeed they have even been employed as active rods in laser cavities [9] and as biochemically active sol–gel glasses [10]. It seemed worthwhile, therefore, to find out whether these matrices might be used to produce dispersed liquid crystal droplets. The pore size distribution of a xerogel varies widely depending on the conditions during gel formation and may be tightly controlled with the chemical composition of the starting mixture [11].

We have recently started a study on the feasibility of using sol–gel techniques to trap droplets of liquid crystals, thus producing thin films of gel–glass dispersed liquid crystals (GDLC). These materials might have, in principle, the same performances as

---

* Author for correspondence.

PDLCs, with the advantage of an improved substrate, for both optical and mechanical properties. Once the formation of droplets inside the glass was achieved, we have investigated several monomers and mixtures under different reaction conditions, in order to vary the pore size and surface properties of the silica cages. GDLCs have been prepared with these matrices using different liquid crystals. The aim of this preliminary work is the selection of the best matrix/liquid crystal combination to use eventually in the manufacturing of specific devices.

The following liquid crystals have been tried: K15 (Aldrich), E7 (BDH), MBBA (EGA-Chemie), Phase 5 (Merck) (all nematics); the cholesteric cholesteryl linoleate (ChL, Eastman Kodak), and the ferroelectric smectic C mixture ZLI-3775 (Merck). All of them but ChL and MBBA (which probably hydrolysed) have yielded droplets of different sizes in several gel–glasses used in the early stages of the work; therefore ChL and MBBA were rejected for the moment, and subsequent experiments were performed on K15, E7, Phase 5, and ZLI-3775.

The samples were given a planar shape by performing the polymerization reaction on a glass plate. This plate was coated with indium/tin oxides to allow the testing of electrical switching. Once the reaction was finished and the material had hardened, a second indium/tin oxide coated glass was placed on the opposite surface and the sample was sealed. In this way, no deformations of the GDLC droplet shapes are induced in the process. This standard procedure was used for the preparation of all samples studied in this work. Sample thicknesses from 0·02 to 1 mm have been obtained; these thicknesses were measured either mechanically (thick samples) or interferometrically (thin samples). In the second case, an air gap between the glass plates near the sample edges was used (the glass plates were larger than the sample). The droplets were observed using a Zeiss polarizing Ultraphot II microscope.

A simple wave generator giving frequency-variable pulse trains of 40 kHz AC square and sinusoidal waves up to 700 V_{eff} has been designed to test the switching and threshold voltage. The threshold was measured by observing microscopically the polarization texture changes of average size droplets for each sample. Transmission was studied on an optical bench equipped with a 10 mW He–Ne laser, 5 × collimator and a large area photodiode to collect the transmitted light into a digital oscilloscope. This setup, with some extra lenses, allows us to probe sample areas from 1 cm^2 down to a few μm^2. The switching time was measured as the time elapsed between 10 per cent and 90 per cent of light transmission variation. In the results given here, no extra lenses were employed, i.e. a quasi parallel beam with or without collimator was used, the explored area being about 1 cm^2 or 4 mm^2, respectively.

Either single monomers or mixtures of two monomers were employed to prepare the samples (see table 1). In the second case, one of the monomers has four functionally reactive site leaving groups, whereas the other has only three. The mixtures were prepared in such a way that the concentration of reactive groups is kept constant. In this way the pore size and the polar characterof the silica cage can be controlled. Details of the synthesis procedure have been published elsewhere [12, 13]. The reactions were performed at room temperature with the reaction times ranging from several hours to several weeks. They are closely related to the starting monomer and its reactivity. Faster processes are being investigated. In a few case, samples were slightly heated (60°C, 3 h) after gelation of the material. This treatment reduces the pore size and the threshold, as shown in table 1.

GDLCs were obtained for most of the matrices and liquid crystals tested. Droplets ranging from 2 to 200 μm were observed by optical polarized microscopy. Droplets

Table 1. Glass dispersed liquid crystals prepared in this study. Monomers are SiR_4 and SiR_3R', where R is a reacting group and R' is a non-reacting group.

Non-reacting group	Reacting group	Liquid crystal (*a*) (conc.)	Reaction time/h	Droplet size/μm	Threshold/ V_{eff} μm^{-1}
None/ CH_2CH_3 (*b*)	OCH_2CH_3	K15 (1·75)			
10/0			290	(*c*)	—
9/1			340	(*c*)	—
8/2			460	20–50	0·35
7/3			460	10–40	0·13
6/4			770	30–80	0·21
5/5			770	10–40	0·18
4/6			1060	20–80	0·60
3/7			1060	20–80	—
2/8			770	20–100	0·26
1/9			> 1500	(*d*)	—
0/10			> 1500	(*d*)	—
		Phase 5 (1·75)			
10/0			240	(*c*)	—
8/2			340	(*e*)	—
6/4			720	20–180	0·23
4/6			960	20–150	0·33
2/8			910	20–130	0·59
0/10			> 1500	(*d*)	—
CH_3	$OOCCH_3$	ZLI-3775	35	2–5	—
CH_3	$OOCCH_3$	K15			
		(0·33–1·0)	15	(*e*)	—
		(1·33)	15	< 1 (*g*)	3·09
		(2·00)	15	1–2	2·36
		(2·67)	15	2–10	1·77
		(3·33)	15	10–12	1·63
		(4·00)	20	10–60	0·59
		(5·33)	20	20–60	1·41
		(6·67)	20	20–60	0·88
		(5·00)	20 (*b*)	10–15	0·25
		(6·67)	20 (*b*)	10–12	0·26
		(10·0)	20 (*b*)	10–12	0·32
CH_3	$OOCCH_3$	E7			
		(5·00)	20 (*b*)	10–15	0·25
		(6·66)	20 (*b*)	5–10	0·20
		(10·0)	20 (*b*)	10–20	0·15
C_6H_5	$OOCCH_3$	K15			
		(10·4)	20	< 1 (*g*)	0·21
		(14·6)	20	< 1 (*g*)	0·10

(*a*) Concentration is expressed in ml liquid crystal per mol of reacting radicals.

(*b*) Mixtures of $Si(OCH_2CH_3)_4$ and CH_3CH_2-$Si(OCH_2CH_3)_3$ were used. Proportions shown.

(*c*) Powder-like sample.

(*d*) No solid final material was obtained.

(*e*) Transparent field in the microscope.

(*f*) After gelation, samples were heated at 60°C for 3 h.

(*g*) No droplets are visible, however a neat switching is detected.

Figure 1.

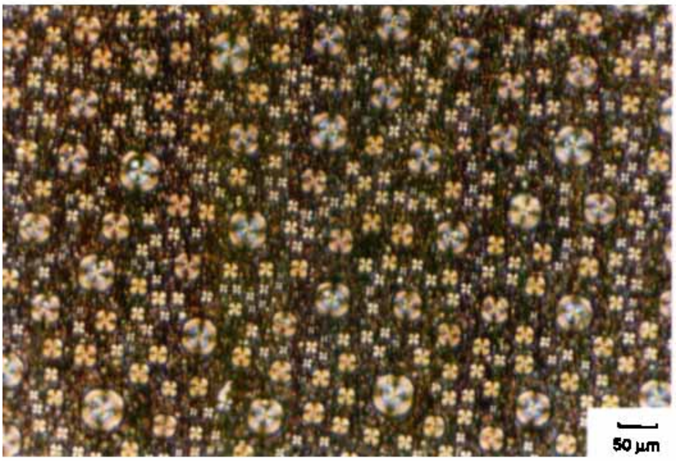

Figure 2.

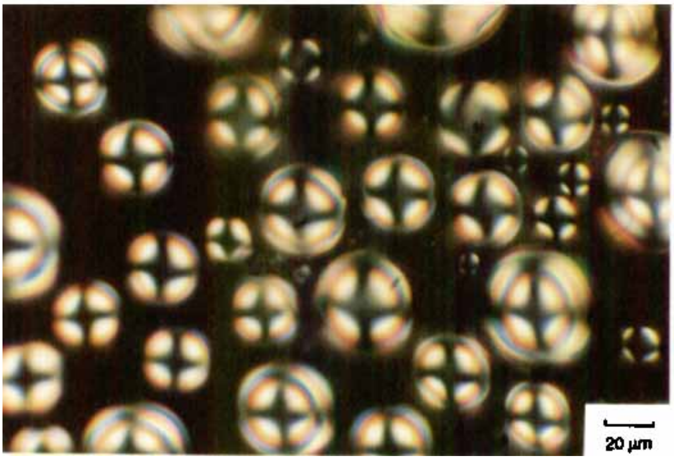

Figure 3.

beyond the resolution power of our microscope ($< 1\ \mu m$) must be present in some cases, as demonstrated by the switching behaviour of several samples. In every single sample, droplet size ranges from 1 : 2 to 1 : 10 were found. Except for a few irregular droplets formed near the sample surface in some cases, all of the droplets were almost perfectly spherical (see figure 1). In addition, a few samples show full coloured patterns with no visible droplets although some of them exhibit switching like usual samples.

As shown in table 1, large variations in reaction times, thresholds and droplet sizes were found. Mixtures of three and four functionally reactive groups yield powder-like samples for the highest concentrations of tetrafunctional monomer and non-solid gum-like samples for the lowest. Neither of these extreme cases could be characterized. Single monomer matrices using a different reacting group were formed in all cases. It must be noted that the chemical composition of the pore walls is different in every case; we believe that most of the observed variations in GDLC formation and behaviour may be attributed to this.

Reorientation of the droplets was achieved with electrical and optical fields. An Ar^+ laser focused onto the sample [12] produces several diffraction patterns which have been previously described in planar and cylindrical liquid crystal samples [14–16]. This feature was observed in dielectrically positive and negative nematics, as expected. Reorientation of negative materials on applying a voltage was observed by evolution of the polarization textures under the microscope. No reorientation was detected in the ferroelectric liquid crystal (with either AC or DC pulses); this fact is presently under study. It is possible that some of the ZLI-3775 mixture components were separated or decomposed during the sol–gel process.

Positive nematics show switching to the naked eye. Macroscopically, the films scatter light strongly in the unexcited state, becoming more transparent when an electric field is applied. No attempt has yet been made to match the refractive index of the matrix ($\sim 1{\cdot}43$) with the ordinary index of the nematic; therefore complete transparency is not achieved for the moment (e.g. T_{ON} about 10–20 per cent), and the contrast is poor (about 5–10 : 1). Nevertheless, it has been demonstrated [17] that the refractive indices of gel–glasses may be modified by introducing some dopants in the polymerizing matrix. This is one of our current research projects.

When observed between crossed polarizers, the droplets appear to be single domains in all sizes but the largest ones. If no voltage is applied, Maltese crosses are observed in most cases (see figures 2 and 3). These pictures are assigned [18] to a radial configuration known as a hedgehog [19, 20]. A few examples of axial configurations, still to be confirmed, have also been found. In the inner surface of the pore, homeotropic orientation is achieved, the direction always pointing to the centre of the sphere. Discontinuities are present at the centre (radial) or at the equator (axial). Stability regions for radial and axial structures depending on the anchoring strength and the pore size have been described [21].

Table 2 shows some examples of switching times. Switching times from several milliseconds to hundreds of milliseconds have been measured (see figure 4). It has been

---

Figure 1. Microscopic view of a glass dispersed liquid crystal sample. K15 droplets in polymerized CH_3–Si $(OOCCH_3)_3$.

Figure 2. Glass dispersed K15 droplets (20–60 μm) between crossed polarizers. Maltese crosses attributed to radial (hedgehog) structures are seen for all sizes.

Figure 3. Polarization texture obtained in glass dispersed E7 droplets.

Table 2. ON and OFF switching times of some K15 samples dispersed in polymerized CH_3–Si $(OOCCH_3)_3$.

Liquid crystal conc. (*a*)	Sample thickness/μm	Applied voltage V_{eff}/V	$t_{ON(10-90)}$/ms	$t_{OFF(10-90)}$/ms
10·00 (*b*)	330	195	15	85
5·00 (*b*)	210	140	10	80
3·33	70	185	3	13
2·00	60	160	12	65
3·33	20	175	6	12

(*a*) Concentration is expressed in ml liquid crystal per mol of reacting radicals.
(*b*) After gelation, samples were heated at 60°C for 3 h.

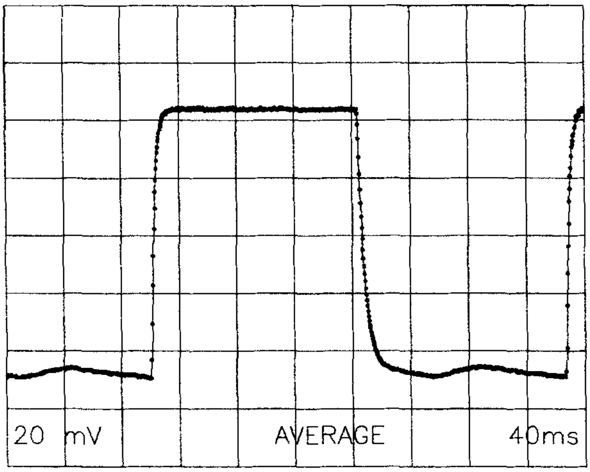

Figure 4. Dynamic response of glass dispersed K15. $t_{ON(10-90)}$ and $t_{OFF(10-90)}$ are 3 ms and 13 ms, respectively.

shown in PDLCs that transverse elongation of the droplets may reduce the switching time dramatically. The use of this technique in GDLCs is presented under study. In that case, other structures like biaxial liquid crystal structures known as boojums [20] may be favoured energetically their orientation being imposed by the longer axis of the ellipsoid; the director is then anchored tangentially to the pore wall.

To the best of our knowledge, the trapping of liquid crystal droplets in inorganic gel-glasses has not been reported previously. These GDLC materials open new possibilities to PDLCs, taking advantage of their excellent optical properties. Obviously, much work has yet to be done to characterize and optimize GDLCs in order to produce practical devices. In any case, even these preliminary results are quite encouraging, opening several promising lines of research in this field.

The authors are indebted to J. M. S. Pena and F. Olarte for their helpful discussions, and to Dr A. Pinillas for the microscopy. This work has been supported by TIC 89/0171 and MAT 90/0791 projects of Spanish Comisión Interministerial de Ciencia y Tecnología (CICyT). A. S. and D. L. thank CICyT for a research grant.

References

[1] Fergason, J. L., 1985, *SID Int. Symp. Digest Tech. Papers*, **16,** 68.

[2] Drzaic, P. S., 1990, *Inform. Disp.*, **6,** 15.

[3] Kunigita, M., Hirai, Y., Ooi, Y., Nirayama, S., Asakawa, T., Masumo, K., Kumai, H., Yuki, M., and Gunjima, T., 1990, *SID Int. Symp. Digest Tech. Papers*, **21,** 227.

[4] Drzaic, P., 1990, *SID Int. Symp. Digest Tech. Papers*, **21,** 210.

[5] Brinker, C. J., and Schere, G. W., 1990, *Sol–Gel Science* (Academic Press).

[6] Avnir, D., Levy, D., and Reisfeld, R., 1984, *J. phys. Chem.*, **88,** 5956.

[7] Levy, D., and Avnir, D., 1988, *J. phys. Chem.*, **92,** 4734.

[8] Levy, D., Einhorn, S., and Avnir, D., 1989, *J. non-crystalline Solids*, **113,** 137.

[9] Reisfeld, R., Brusilovsky, D., Eyal, M., Miron, E., Burstein, Z., and Ivri, J., 1989, *Chem. Phys. Lett.*, **160,** 43.

[10] Braun, S., Rappoport, S., Zusman, R., Avnir, D., and Ottolenghi, M., 1990, *Mat. Lett.*, **10,** 1.

[11] See [5], chaps 2 and 9.

[12] Levy, D., Serna, C. J., and Otón, J. M., 1991, *Mat. Lett.*, **10,** 470.

[13] Preparation and applications of GDLCs are patent pending (9101325E).

[14] Durbin, S. D., Arakelian, S. M., and Shen, Y. R., 1981, *Phys. Rev. Lett.*, **47,** 1411.

[15] Otón, J. M., Beltrán, R., and Martín-Pereda, J. A., 1985, *Molec. Crystals liq. Crystals*, **127,** 43.

[16] Menéndez-Valdés, P., and Martín-Pereda, J. A., 1987, *Molec. Crystals liq. Crystals*, **149,** 303.

[17] Yamane, M., Kawazoe, H., Yasumori, A., and Takahashi, T., 1988, *J. non-crystalline Solids*, **100,** 506.

[18] Bellare, J. R., Davis, H. T. Miller, W. G., and Scriven, L. E., 1990, *J. Colloid Interf. Sci.*, **136,** 305.

[19] Kralj, S., Vilfan, M., and Zumer, S., 1989, *Liq. Crystals*, **5,** 1489.

[20] Doane, J. W., 1991, *Mat. Res. Soc. Bull.*, **16,** 22.

[21] Erdmann, J., Zumer, S., and Doane, J. W., 1990, *Phys. Rev. Lett.*, **64,** 1907.