Articles

Surface Organic Modifications and the Performance of Sol−Gel Derived Gel−Glass Dispersed Liquid Crystals (GDLCs)

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A new and reliable formulation has been developed for the preparation of gel−glass dispersed liquid crystal (GDLC) thin films using the sol−gel technique. Liquid crystal (LC) droplets were formed in-situ during the drying process of the applied films. Tetraethoxysilane (TEOS) and different triethoxysilanes (R-TES) were used as precursors for the preparation of gel−glass−LC composites resulting in silica or organically modified silica matrixes (Ormosils). The usage of different precursors resulted in GDLCs with different electrooptical behavior due to the anchoring strength of the matrix surface to the LC molecules in the droplets. Samples prepared from TEOS or mixed TEOS/Me-TES precursors showed switching times between ON and OFF states of 10 and 300 ms, respectively, and required peak-to-peak voltages (V_{p-p}) of 200−300 V for operation. On the other hand, samples using TEOS/Et-TES and TEOS/Pr-TES precursors mixtures required much lower activation voltages of 100 and 40 V, respectively, and exhibited a very slow electrooptical response ranging between 1 and 3 s.

Introduction

Polymer-dispersed liquid crystal materials (PDLC's) were first reported by Fergason[1] and consist of a dispersion of LC microdroplets in solid polymer matrixes.[2,3] The LC molecules in a droplet adopt a long-range orientational order along a director, which is different for each droplet. The LC droplets, dispersed in a transparent matrix, scatter the incident light providing an opaque layer (OFF state). Upon application of an external electric field, the birefringent LC molecules inside the droplets undergo a reorientation, changing the refractive index of the LC droplets in the direction of the light path to match that of the matrix. In the ON state, therefore, a transparent composite is obtained. These materials are of an increasing interest for their application as electronic displays (LCD), optical switches, or light modulators.[4,5] The possibility to prepare large-area PDLC devices is gaining interest for the decorative glass industry, where intelligent windows based on this type of light modulators are being produced.[6] Among other advantages, PDLCs need no polarizers for operation, and no surface treatment is required to scatter light in the OFF state. Many efforts have been devoted lately to the development of PDLC devices in order to control specific electrooptical properties in a thin film.[7−11]

The surface of the matrix where the LC droplets are allocated will be responsible for the anchoring of the LC molecules inside the droplets. This anchoring will force the LC molecules to adopt a director configuration, which is different for each droplet. The anchoring strength will depend on the nature of the matrix surface (functional groups) around the droplets. The control of the anchoring strength on PDLC systems has been the subject of numerous works.[12−15] Another important factor to define the performance of a PDLC is the size of the LC droplets dispersed in the matrix, as it will

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Table 1. Composition of the Sols Used for Deposition and Main Properties of GDLC Samples

		molar composition of the sol								droplet size			transmittance(%) at 632 nm[a]	
sample	R-TES	TEOS	R-TES	EtOH	H_2O	HNO_3	K15	Si/R	thickness (μm)	d (μm)	σ (SD)	σ/d (%)	OFF state	ON state
S	none	1.00	0	0.75	1.8	0.03	0.075		1.6	0.66	1.18	178	45	86
S/Me	Me-TES	1.00	1.12	1.5	3.6	0.06	0.15	1.89	1.9	0.99	0.76	77	40	88
S/Et	Et-TES	1.00	1.03	1.5	3.6	0.06	0.15	1.97	1.6	0.66	0.26	39	71	98
S/Pr	Pr-TES	1.00	0.96	1.5	3.6	0.06	0.15	2.04	1.8	1.02	0.23	23	87	94
S/Bu	Bu-TES	1.00	0.89	1.5	3.6	0.06	0.15	2.12	2.1					

[a] Measured vs clean ITO reference plates.

determine the contact surface between the LC and the matrix, and hence, the anchoring of the LC molecules.[16]

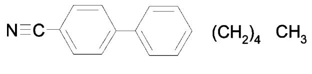
The ability of entrapment of organic molecules into inorganic matrixes[17] opened a wide range of possibilities in the field of optical and electrooptical devices. Recently, the sol−gel process has been used to produce LC microdroplets into gel−glass matrixes (gel−glass dispersed liquid crystals, GDLC).[18−20] These new composites offer better transparency and thermal stability than PDLC and a larger difference between the refractive indexes of the matrix and the LC droplets, leading to higher light scattering in the OFF state. Since the first works published on GDLCs,[21−22] efforts were oriented to improve the performance of the prototype devices using different sol−gel silica precursors,[18,21] amino silicon alkoxides,[23] or titanium oxide precursors.[20,24] Another important advantage of the sol−gel method is the possibility to control the properties of the porosity, such as size and chemical environment, in which the liquid crystal will be allocated. This can be done using ormosils ($RSi(OR')_3$) to obtain organically modified silica matrixes. The non-hydrolyzable organic substituents of the ormosil (R) will remain in the surface of the pores defining its properties.[25] The ability to control the pore surface properties of the host matrixes as well as the size of the LC droplets will be of great importance, as it will allow tailoring the performance of the GDLC device. Despite the good possibilities offered by the sol−gel method for the preparation of GDLCs, the sols used for film deposition exhibited very low viscosity stability, making the deposition of films difficult and hardly reproducible. Moreover, the resulting films exhibited wide droplet size distributions and hence low homogeneity in the properties of the LC droplets.

It is important, in order to study these materials, to find new routes for the preparation of the samples. The aim of this work is to find an alternative chemical formulation of a sol for the preparation of reproducible GDLC films. The most important preparation parameters will be studied and optimized in order to obtain GDLC samples from rather stable sols, which in turn, will allow good reproducibility and the optimization of the GDLC's performance. Among those parameters are the deposition technique, the thickness of the films (possibility of multilayer deposition to increase thickness), and the drying process, consisting mainly of the solvent used and its amount.

The performance of the resulting composite will be controlled by the introduction of different functional groups into the gel−glass matrix. Mixtures of TEOS and R-TES alkoxides ($R = -CH_3, -CH_2CH_3, -CH_2CH_2CH_3$, and $-C(CH_3)_2CH_3$) will be used for the preparation of the matrix where the LC droplets will be allocated. The properties of the pore surfaces will be determined by the ormosil used for preparation. This in turn will strongly affect the anchoring of the molecules inside the droplets and hence, the performance of the GDLC.

Experimental Section

Materials and Compounds. TEOS (tetraethoxysilane) and MeTES (methyl triethoxisilane) were purchased from Aldrich, EtTES (ethyl triethoxisilane) was from Fluka, PrTES (propyl triethoxysilane) and BuTES (butyl triethoxysilane) were from ABCR, ethanol was obtained from Merck, nitric acid was from Panreac, and PBCN (4′-pentyl-4-biphenylcarbonitrile) was from Aldrich. For all preparations double-distilled water was used.



PBCN

Preparation of Sols. The sols used for film deposition consist of a mixture of alkoxides (TEOS and R-TES) with ethanol, acidified water, and liquid crystal. Silicon alkoxides precursors were mixed with EtOH and the corresponding amount of water (as 0.55 M HNO_3) in a ratio given in Table 1. Upon addition of PBCN a phase separation is observed. Miscibility is accomplished as the hydrolysis of the alkoxides proceeds. The clear sols obtained are viscosity-stable for at least 10 days.

Deposition of Films. The GDLC films were deposited by spin coating at 2000 rpm on transparent ITO-coated conductive glasses from Balzers.

Device Preparation. The coated films were used to prepare a sandwich-like all-solid GDLC device using an ITO-coated glass as a second electrode. The two glasses were held together by means of a metallic pinch clamp. Figure 1 gives a schematic representation of the GDLC devices.

Characterization. Microscope photographs were taken by a Leica MPS32 camera attached to a Leica BMRM optical microscope equipped with polarizer and analyzer, using a 100× magnification. The pictures were taken using cross polarizers where only ordered LC domains can be observed. The electric field was applied by an AC power supply generating 20 kHz sinusoidal pulses with a peak-to-peak voltage (V_{p-p}) of 10−400 V. The electric field was applied to samples in intervals

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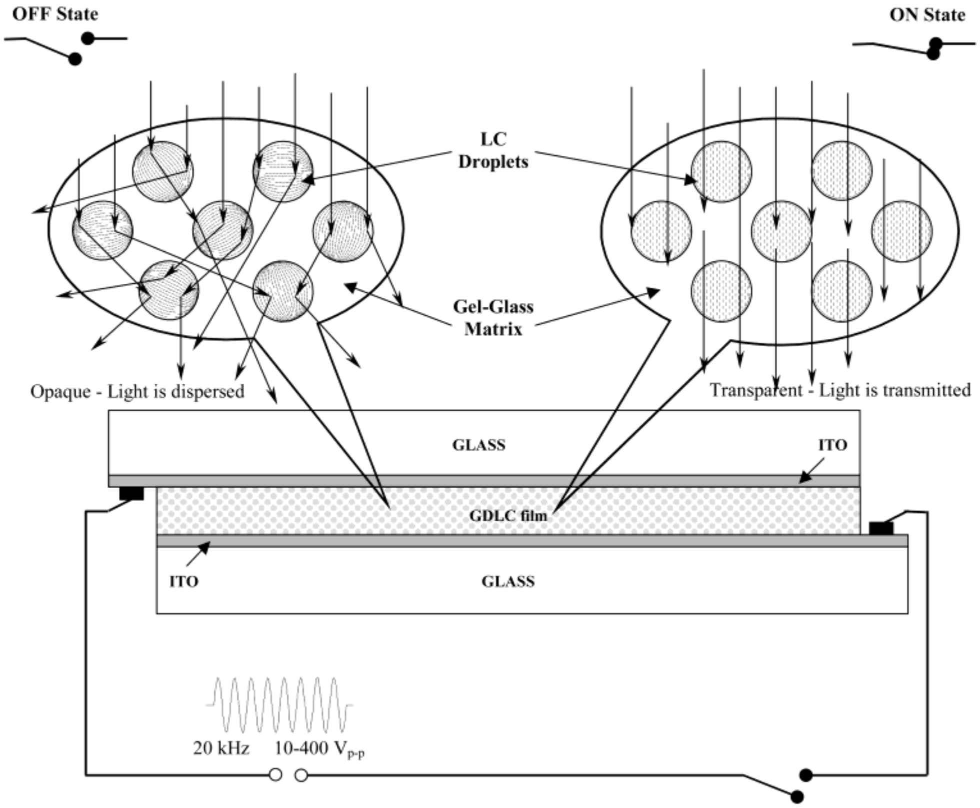

Figure 1. Schematic representation of the GDLC devices.

of 1 s power ON and 1 s power OFF. The switching performance of the GDLCs (rise and decay times) was measured by irradiating the samples with a Uniphase 1125P 10 mW He−Ne Laser (632.8 nm), and measuring the out-coming light by means of a light detector attached to a Tektronix TDS 360 digital oscilloscope. UV−Vis absorption spectra were recorded on a Varian 2300 spectrophotometer while the electric field was applied to the samples. The thicknesses of the films were measured with a Taylor−Hobson Form Talysurf-50 profile analyzer. The particle size distributions were calculated by measuring more than 200 droplets from the microscope photographs.

Results and Discussion

Composition of the Sols. The sols used for film deposition must be clear and stable to allow the preparation of homogeneous films. Upon application of the films on the substrate, a phase separation must occur to obtain small LC droplets (about 1 μm) dispersed on the silica matrix. The composition of the sol, in particular the solvent and silica precursors used, should be designed to make the phase separation coincide with the solidification of the silica matrix. The solvency of the sol is responsible for miscibility of the LC and silica precursor phases, at the same time it prevents the gelation of the sol. The LC molecules in the droplets aggregate to larger droplets until the glass matrix solidifies and confine the droplets on its pores. The faster the glass matrix is formed, the smaller are the resulting LC droplets. The amount of solvent and its evaporation rate, as well as the gelation rate of the sol, will play a decisive role during the formation of the LC droplets. A thorough control over the drying process is essential to control the properties of the resulting films.

The stability of the sols is key to obtaining reproducible films and was therefore defined as one of the aims of this work. Very fast gelling sols (1−2 h) require a thorough control over the temperature of the sol and substrate, to allow film deposition. Moreover, the deposition should be done at a precise time after the precursors are mixed together in order to obtain the desired viscosity (to control film thickness). It was important therefore, to find a sol which is viscosity-stable for at least one week at room temperature to allow repeatability and reproducibility of the results.

The ormosil used for preparation of the GDLC samples, especially the nature of the non-hydrolyzable organic group of the alkoxide precursor, also plays an important role in the formation of the LC droplets. It is known that during glass formation these organic groups are oriented toward the pore cavities where the LC molecules will be allocated. Therefore, the size of the organic substituents and its affinity to the LC molecules will affect the size of the pores and the LC loading admitted by the specific matrix. Moreover, the incorporation of nonreacting organic substituents into the pores leads to the preferential confinement of the LC molecules into the pores rich in organic substituents due to the chemical affinity and size/volume considerations. In sample S, the lack of organic substituents led to the aggregation of the droplets, resulting in a very wide size distribution. The shrinking of the matrix in sample S could not be limited by the organic groups resulting in the exudation of the LC molecules to the outer surface of the layer due to the low pore volume of the resulting matrix. TEOS was used in all preparations as a co-precursor to keep the same basic structure in all matrixes and obtain more stable sols. The compositions of the sols used were designed taking into consideration the above-described issues. The consecution of the new formulation is of great importance to allow a deep study of the GDLC systems, as it allows a reproducible preparation of thin films with LC-droplets dispersed in a low-organic ormosil matrix. Moreover, the formulation found admits the incorporation of different organic substituents in the form of ormosils co-precursors, which modify the pore surface, where the LC molecules are allocated. This, in turn, allowed control over the anchoring strength of the resulting matrix and the electro-optical properties of the GDLC devices.

Preparation of Films. The films prepared in this work were prepared using the spin-coating technique. Thin layers of about 2-μm thickness are obtained for all sol compositions. The films are quickly dried, forming small (0.3−2 μm) LC droplets. S and S/Me samples exhibited wide size distribution, whereas samples S/Et and S/Pr showed a very narrow size distribution. Thicker films (up to 15−20 μm) were prepared using other deposition techniques such as dip-coating or spreading a drop of the sol on the glass substrate. The slow drying of these films resulted in a large aggregation of the LC droplets, a very wide droplet size distribution, and a drastic reduction in film quality, and were therefore, not included in this work.

The possibility of multilayer GDLC films was explored. Successive layers were deposited allowing the sample to dry at room temperature for 24 h after the application of each layer. The resulting samples exhibited thicker films but showed no improvements in GDLC performance over that of single layer films. Multilayer samples in OFF-state have higher opacities and wider LC droplet size distributions. Because of their increased thickness, the samples require higher voltages for operation and exhibited a lower optical quality. For these reasons, the results of multilayer samples will not be presented in this work. However, because of the important advantages of a thicker GDLC film, the possibility of multilayer films will probably be a matter of a future work.

Droplet Size. Samples prepared with different triethoxysilanes showed remarkable differences in droplets size and distribution. Optical microscopy pictures of the LC droplets in gel−glass matrixes for samples S, S/Me, S/Et, and S/Pr are presented in Figure 2. Samples S and S/Me showed a large dispersion in droplet size and a certain amount of LC exuded in the surface. S/Et and S/Pr samples, however, showed a much larger homogeneity in droplet size and no LC in the outer surface of the matrix. The average size and size distribution of the LC droplets in the different samples are summarized in Table 1. The ormosil used for sample preparation has an important effect on the size of the pores and LC droplets in the matrix, as well as the amount of LC the matrix is able to allocate. Moreover, the organically modified pores constitute a preferential site for the formation of the LC droplet due to chemical affinity and space considerations. Matrixes prepared using larger organic substituents lead to structures with larger pores, resulting in the formation of larger LC droplets and an overall higher amount of LC in the matrix. Matrixes prepared with no organic substituents have no preferential sites for allocating the LC molecules and the size of the droplets will depend on the amount of LC in the sol. If the amount of LC in the sol is too high, the LC will be exuded to the surface of the layer during the matrix formation and drying. On the other hand, if the amount of LC in the sol is too small, the result will

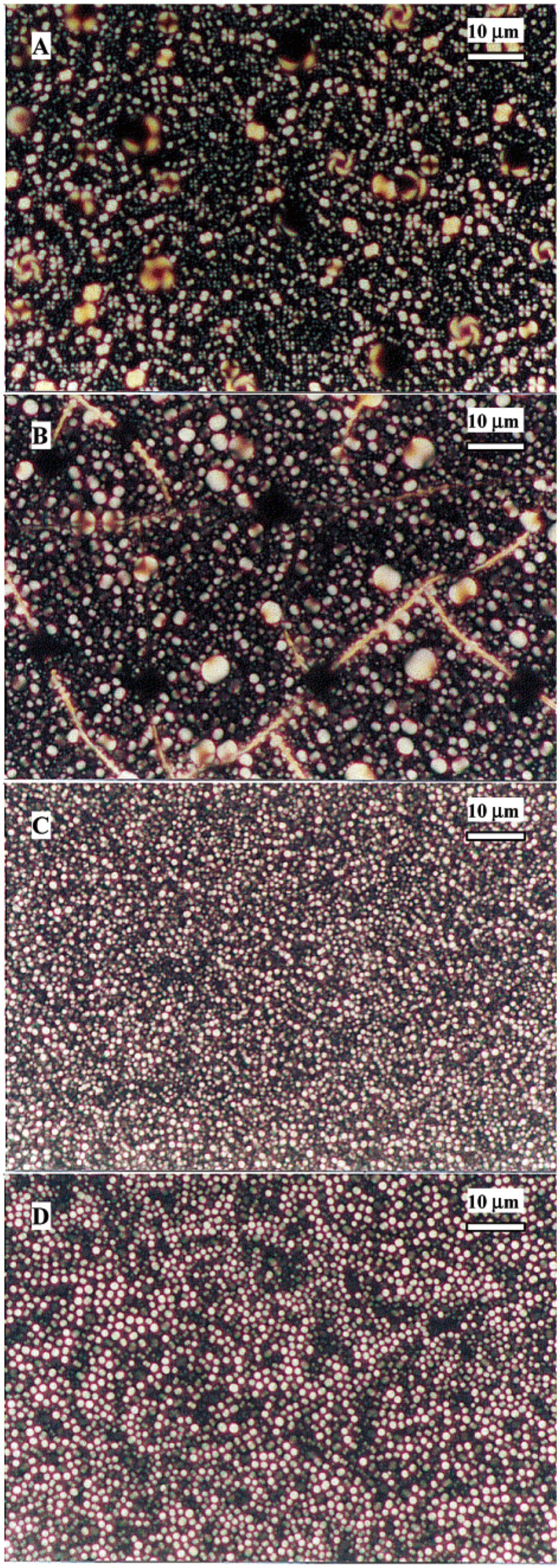

Figure 2. Microscopy pictures showing the LC droplets inside the different gel−glass matrixes: (A) sample S; (B) sample S/Me; (C) sample S/Et; and (D) sample S/Pr. Samples were observed through crossed polarizers.

be very small LC droplets dispersed in the matrix pores or even a dispersion of single LC molecules in the glass matrix. Because the performance of the GDLC is proportional to the amount of LC in the resulting film, the LC concentration should be taken to the maximum allowed by the specific matrix.

Dynamic Response. The LC molecules in a droplet adopt a director orientation, due to their anchoring to the surface of the pores, which is different for each droplet. In this situation (OFF state) the layer scatters light and is therefore opaque. Upon application of an electrical field (ON state) the layer becomes transparent, due to the reorientation of the LC molecules in the direction of the applied field, recovering its opacity upon removal of the field. The dynamic response of a GDLC depends on the ability of the LC molecules inside the droplet to abandon their director orientation and reorient themselves in the direction of the applied electrical field. The surface of the matrix pores is responsible for anchoring of the LC molecules in the droplet. The applied electric field must overcome the anchoring strength of the molecules in the droplet to align the molecules in the direction of the field and exhibit the electrooptical effect. Both the rise time (t_{on}) and the decay times (t_{off}) depend on the anchoring strength, however, the rise time depends also on the voltage applied for operation. The stronger the anchoring produced by the matrix, the faster the molecules will recover their original orientation and the opacity of the GDLC layer. At the same time, strong anchoring conditions will require higher threshold voltage (V_t) to make the molecules move inside the droplet. Once the V_t is achieved, faster t_{on} is observed for higher applied fields. Figure 3 shows the raising and decay rates for samples S, S/Me, S/Et, and S/Pr. The value of t_{on} measured at 200 V_{p-p} for all samples was found to decrease for larger organic substituents, while t_{off} measured at no applied field was largely increased. These results show that the anchoring strength of the matrix decreases as larger organic substituents are used. As mentioned before, the rise time depends also on the applied voltage. Figure 4 shows the dynamic response of samples S, S/Me, and S/Et at different driving voltages. As shown in the figure, the rise time of sample S/Et is much slower than those of samples S and S/Me. However, this effect is only attributable to the much lower voltage required for activation. If the same voltage is applied, faster rising times are achieved with S/Et, due to the weaker anchoring forces observed in this sample (see Figure 3). Above the V_t, all samples exhibited an increasing light transmission for stronger applied fields. Samples with stronger anchoring strength showed higher saturation voltages V_{sat}, as shown in Figure 5. The highest V_{sat} of about 400 V_{p-p} was found for sample S, while the lower V_{sat} of about 40 V_{p-p} was found for sample S/Pr. In both cases the samples have an approximated thickness of 2 μm.

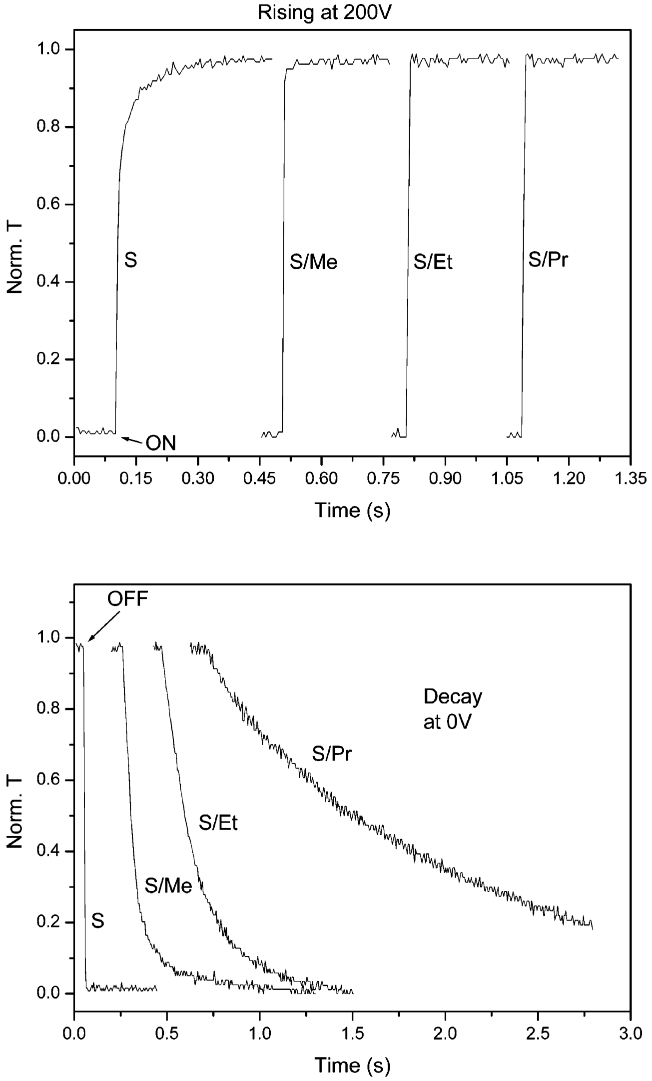

Figure 3. Dynamic response of GDLC devices: (A) rising (activation) at an applied electrical field of 200 V_{p-p}. (B) decay (relaxation) at 0 V.

The dynamic response of the GDLC devices presented here can be explained by the decreasing anchoring strength obtained as larger R groups are used to prepare the samples. In silica matrixes, the resulting droplet–matrix interface is composed mainly of OH groups bonded to the silica network. These polar groups give rise to electrostatic forces between the surface and the droplet resulting in a strong anchoring of the LC. In ormosil matrixes, the organic substituents are oriented toward the pores and hence toward the LC droplets. The presence of aliphatic nonpolar groups at the surface of the matrix reduces the anchoring forces to the LC molecules in the droplets. In addition, the organic groups can hinder the electrostatic forces between the LC droplets and the OH groups on the silica surface. This can also explain the fact that the S/Bu sample is not opaque in its OFF state. The very weak anchoring forces of the S/Bu matrix cannot induce the molecules in the droplet to adopt a director configuration, resulting in a homeotropic orientation of the molecules inside the droplet, with the sample therefore being transparent to the incident light.

The light absorption of GDLC devices in the UV–Vis range of the spectra is mainly due to the scattering of light, and depends therefore on the wavelength of the incident light.[26] Upon application of the electric field the light scattering is strongly reduced and the films become transparent. To obtain fully transparent films a refrac-

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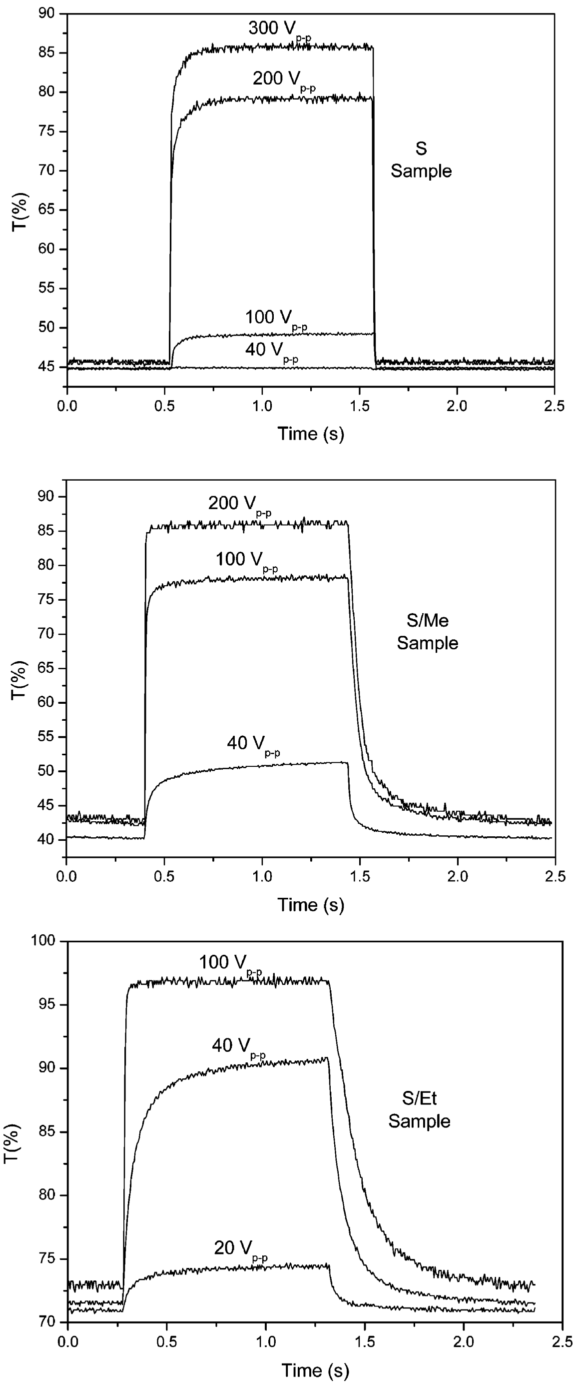

Figure 4. Dynamic response of GDLC devices at different driving voltages.

tive index matching between the matrix and the LC droplet in the ON state is required. Figure 6 shows the absorption spectra of the GDLC sample S while switching the device between ON and OFF states. The maximum ΔT of about 30% was observed at 480 nm, corresponding to a contrast value (T_{ON}/T_{OFF}) of about 1.8. This value can probably be improved by deposition of thicker films (multilayer) or modifications of the matrix composition to achieve better index matching between the matrix and the LC in the ON state.

Conclusions

In this work, a reliable method was found for the preparation of gel−glass dispersed liquid crystals (GDLC) films. Microdroplets of 4′-pentyl-4-biphenylcarbonitrile (LC) were dispersed in an ormosil gel−glass matrix prepared from tetraethoxysilane, or methyl-, ethyl-, propyl-, or butyl-triethoxysilanes. One of the most important achievements of this work is the formulation of the precursor sols used for films deposition, which is stable for at least 10 days, allowing repeatability and reproducibility of the results. This new formulation is the result of a successful blend of precursors, LC, and solvent, to obtain a phase separation (LC-droplets/matrix) during the formation of the gel−glass, immediately after the deposition of the film. Using this new procedure thin GDLC layers of about 2 μm were obtained, which are much thinner than those reported in the literature, typically between 20 and 50 μm, and exhibit similar electrooptical responses.

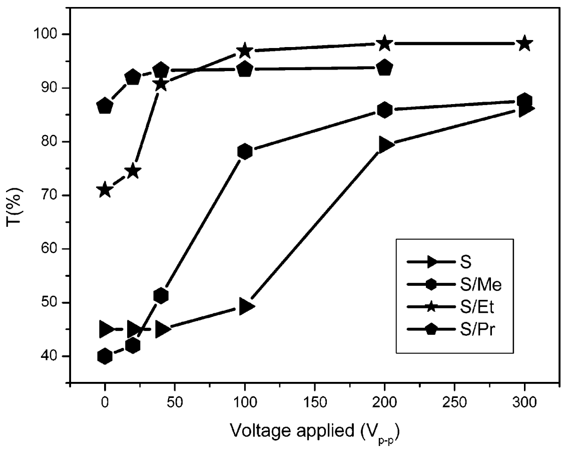

Figure 5. Light transmittance of the GDLC devices as a function of applied voltage.

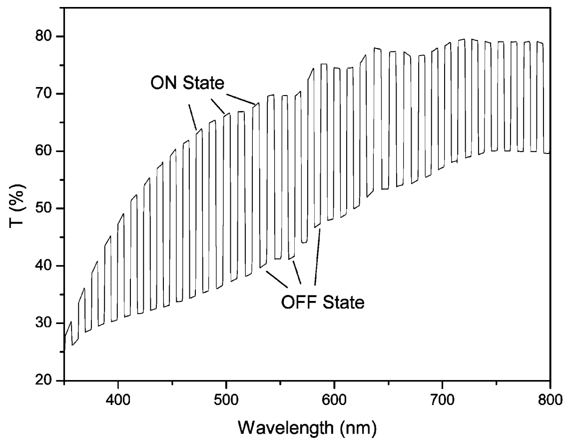

Figure 6. UV−Vis transmission spectra of S sample during ON−OFF states switching at an applied electrical field of 200 V_{p-p}.

Using organic substituents in the glass matrix was found to have a direct and most important influence on the performance of the GDLC devices. The anchoring strength of the glass matrix to the LC molecules in the droplets decreased drastically as larger organic substituents were used, showing a decreasing opacity in the OFF state, requiring lower driving voltages for operation and exhibiting much slower relaxations as compared with those of samples prepared in a silica matrix. The resulting composite GDLC films exhibited droplets ranging from 0.3 to 2 μm, with a quite narrow size distribution, especially in larger substituents ormosil matrixes. These narrow size distributions will allow the study of the anchoring mechanism in the GDLC, as it depends strongly of the size of droplets.

This new preparation procedure will now be used to optimize the composition of the matrix, incorporating active organic groups into the pores' surfaces to allow a chemical control of the performance parameters of the GDLC devices.

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