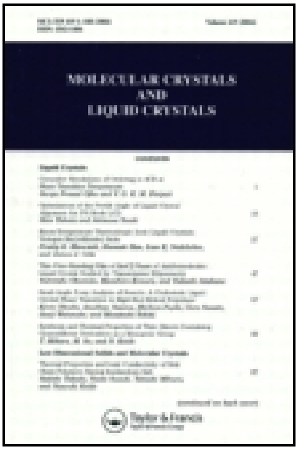


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# Optical Storage Effect in Dye Doped Polymer Dispersed Liquid Crystals

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# Optical Storage Effect in Dye Doped Polymer Dispersed Liquid Crystals

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We report an accurate analysis of an optical storage effect observed in dye-doped PDLC films. Permanent diffraction gratings are produced using standard holographic techniques with different kind of PDLC samples. For all these samples the polymerisation process is completed before the writing procedure. The analysis of the experimental results brought us to distinguish the role of the PDLC components in the observed phenomenon and propose some hypothesis about the possible physical mechanisms at the basis of the storage effect.

Keywords: optical storage; dye; polymer dispersed liquid crystals

## INTRODUCTION

In the last years a great interest is grown concerning the studies of new optical storage materials[1-6]. Many papers have been published on synthesis and characterisation of materials in which holographic storage effect mechanisms are different. In particular, holographic grating formation has been studied in doped nematic[5], polymeric liquid crystals[7] and PDLC with photopolymers[8,9].

Persistent gratings are observed in doped PDLC [10,11], these gratings are obtained by a few seconds exposition to an interference light pattern on samples already cured. The reversibility of the writing process is due to this feature. In fact these structures can be erased using a uniform irradiation from one of the two writing laser beams and then rewritten in the same region. This cycle can be repeated many times without any damage of the samples. Moreover, applying an external voltage, which orient the liquid crystals inside the droplets, it is possible to produce a modulation of the diffraction efficiency of the gratings. In our work we report a wide analysis of the holographic gratings written on dyed PDLC films. Different kinds of PDLC are used, based on thermoplastic polymers and epoxy resins both in which the polymerisation process was concluded before the laser irradiation. Two type of dye was used: an azo-dye and an anthraquinone one in order to investigate the effect of the dye in the process. In fact, as well known, during the writing, the interference patterns replicate in the medium as a change of absorption coefficient, refractive index, thickness or density. It is clear that since the PDLC are multi-component material several physical mechanism may be responsible of the storage effect and it is necessary to distinguish the role of the different components. The optical characteristics of the gratings are investigated for PDLC having different components and the same dyed polymers. Scanning electron microscope (SEM) measurements are performed to investigate the morphology of the sample irradiated by the intensity interference pattern.

Our results allow us to make the following hypothesis about the type of grating produced: a refractive index modulation due to a liquid crystal orientation inside the droplets in alternating regions.

## EXPERIMENT

In order to produce and observe the permanent gratings a standard experimental geometry has been utilised. The PDLC sample was placed in the interference region of two $Ar^+$ laser beams which intensity ratio is $I_1 / I_2 = 1/2$ where the light intensity is $I = I_0[1+\cos(\bar{q} \cdot \bar{x})]$, being $\bar{q}$ the grating wave vector. In this way a grating with periodicity $\Lambda = 2\pi / |\bar{q}| = \lambda / [2sin(\theta / 2)]$ was obtained, where λ is the incident radiation wavelength and θ the crossing-angle between the two beams.

Using intensity values of few $W/cm^2$ even for exposure time very long (hours) transient gratings are observed[12]. The permanent gratings are observed only for intensity values, above a particular threshold, ranging from 40 to $10^3$ $W/cm^2$ depending on the exposure time, the kind of PDLC components used (polymer, dye) and their relative concentration. The beams are weakly focused resulting in a spot size on the sample of 600 μm.

The study of the samples were performed by a pump-probe technique, the gratings being revealed by the diffraction of an He-Ne polarised laser beam passing through them. The obtained gratings are reversible and can be modulated by application of an electric field. The erasure takes place in few seconds by a uniform illumination achieved using only one of the two writing beams. The diffracted beams are not present during the writing process but only when the writing beams are removed.

## SAMPLES

In order to investigate the role of different components on the properties of the observed gratings we have prepared PDLC changing one component at a time. The samples used have been realised with two different polymers (epoxy resin and poly-methyl metacrylate, PMMA), two kind of dye (azo-dye, D2 and anthraquinone, D37) and two nematic liquid crystals with different sign of dielectric anisotropy $\Delta\varepsilon$. Two kind of PDLC are obtained depending on the phase separation process. The first one (A) is prepared by polymerization induced phase separation (PIPS), starting from a mixture of nematic liquid crystal (E7 by MERCK), epoxy resins (Epon 815 by Shell Chem., MK107 by Wilmington Chem. and Bostik B by Boston), an initiator (Capcure 3-800) and a dye (the azo-dye D2 or the antraquinone D37, both by MERCK). The second type (B) was obtained by temperature induced phase separation (TIPS), mixing the liquid crystal (E7), the thermoplastic polymer (PMMA), and the dye (D2 or D37) in warm environment. The structures of the two types of samples are quite different, since the former is made by a crosslinked polymer while the latter by a linear chain polymer. The dyes too have distinct properties: D2 is an azo-dye that shows photoinduced cis-trans isomerisation, while the antraquinone D37 doesn't present this effect. The different dyes used allow us investigating the role of the molecular conformation variation on the studied phenomena. About the liquid crystal the first measurements have been made with E7, subsequently from the analysis of the obtained results from all the samples we used ZLI-4788, a nematic having $\Delta\varepsilon<0$. The cells used were 36μm thick and made by conductive glasses.



## RESULTS

Optical investigations of the gratings have been performed measuring the diffraction efficiency. Due to high light scattering of the sample an alternative definition of the diffraction efficiency is applied: $\eta=I_1/I_{tr}$, where $I_1$ is the first diffracted beam intensity and $I_{tr}$ the transmitted intensity. For thin gratings, the diffraction efficiency can be written[13] as $\eta = \left(\frac{\pi \Delta n d}{\lambda}\right)^2 + \left(\frac{\Delta K d}{4}\right)^2$, where $\Delta n$ and $\Delta K$ are the refractive index and the absorption coefficient modulation, respectively. In case we are dealing with a pure phase or amplitude grating it is possible to evaluate $\Delta n$ or $\Delta K$ from the definition of efficiency. The reported measurements are both for s and p probe beam polarisation varying the writing beam intensity and polarisation and the grating pitch too. Transient gratings have been observed for intensity values up to 40W/cm$^2$ for the A type sample and up to 300W/cm$^2$ for the B type, even for exposure time of some hours. These results indicate that the process is much complex than a simple energy dependence. In fig.1 we report the dependence of the gratings efficiencies on the exposure time, written with s polarised beams on samples B.

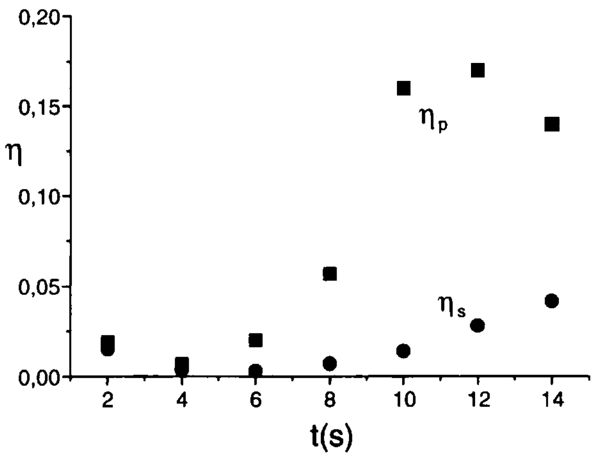



FIGURE 1 Diffraction efficiency versus the exposure time, for an intensity value of 45W/cm$^2$.

Fig.2 and 3 show the efficiencies versus the intensity values for s and p polarised writing beams, respectively, for the sample B with different dyes. Similar behaviour has found for type A sample. The main observation from these measurements is the strong efficiency anisotropy, $\eta_P > \eta_S$, not dependent on the writing beam polarisation. The complexity of the involved processes is interlined by the observation that to get the same values of the efficiency, for different intensities, the energies required must change.

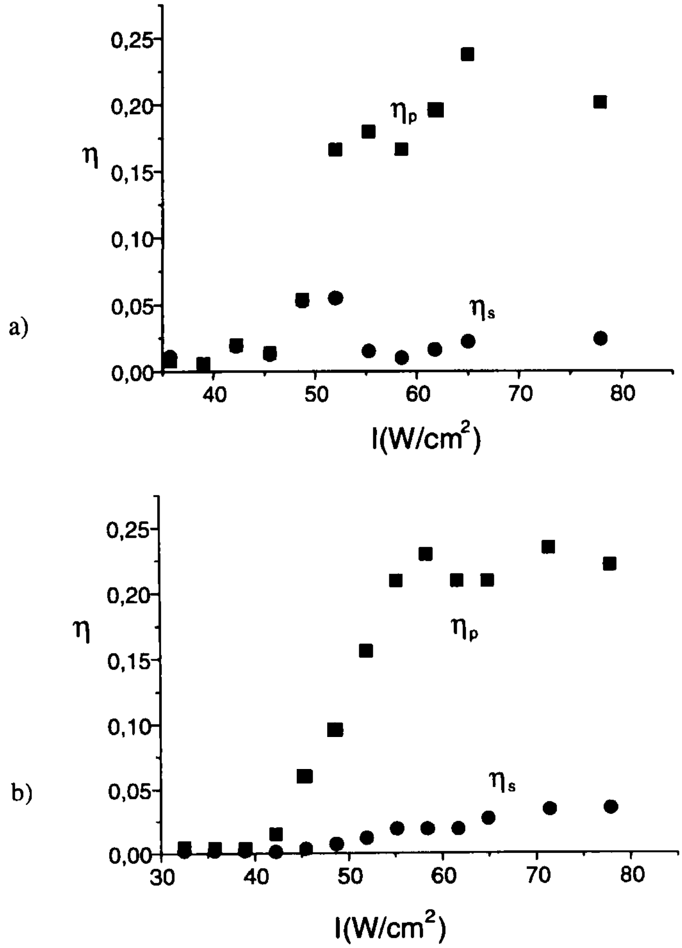
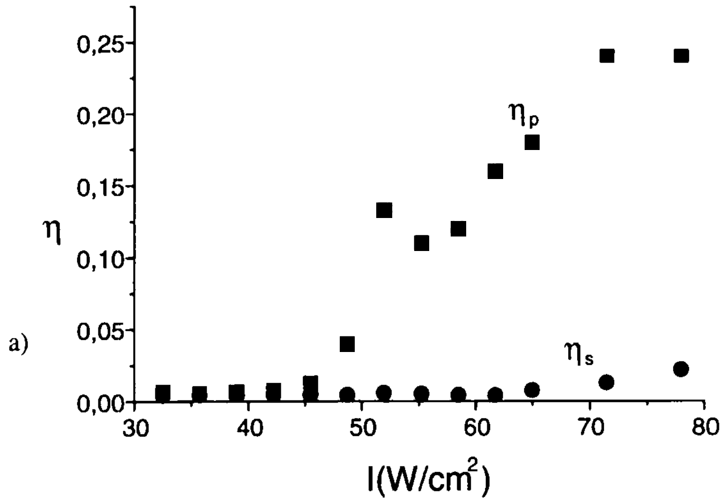



FIGURE 2 Diffraction efficiency versus the writing beam intensity for the sample B doped with dye D2, for p a) and s b) polarisation of writing beams, and an exposure time t=8s.



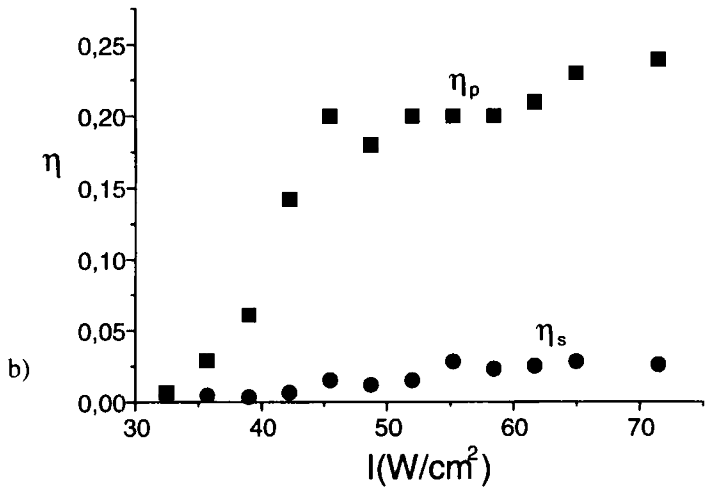
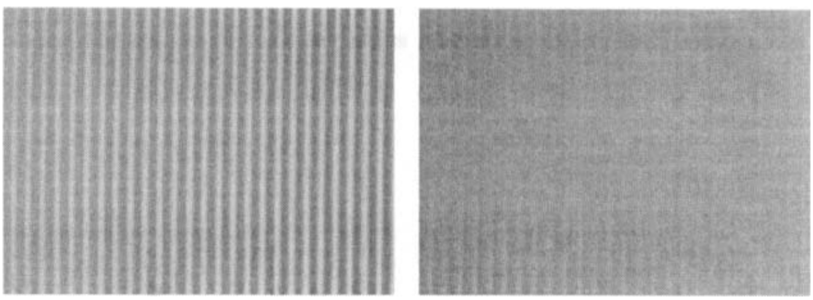




FIGURE 3 Diffraction efficiency versus the writing beam intensity for the sample B doped with dye D37, for p a) and s b) polarisation of writing beams, and an exposure time t=8s.

Fig.4 shows the observation of the grating under polarising microscope. From this picture is evident the anisotropic orientation in written pattern. Experimental results from samples of both kinds show the same strong anisotropy that reach similar efficiency values, using the same liquid crystal, as indicated in table 1. In this table are reported the maximum efficiency values measured on each PDLC sample. For all the samples, changing both polymer and dye the efficiencies values are very close, they differs only in one case but their ratio $\eta_P/\eta_S$ is always the same. Since permanent gratings are observed in dyed polymer samples not including any liquid crystal, we collect the measured efficiency in tab.2. These results are of particular interest to understand the nature of our gratings. The table shows that efficiency is two or three order of magnitude less than the one of PDLC, moreover there is no evidence of the anisotropy as evident in table 1.



a b

FIGURE 4 Optical polarising microscope photographs of the grating. The light polarisation is perpendicular (a) and parallel (b) to the grating lines.

Only for the sample PMMA-D2 the $\eta_S$ value is different from $\eta_P$ but the behaviour is different from the one that characterises the PDLC persistent gratings. In fact the efficiency anisotropy show a clear dependence on the writing beam polarisation and can be easily explained as due to a photoinduced conformational change of the azo-dye hosted in the linear chain polymer. On the contrary, this effect is hindered for the same dye host in the crosslinked polymer. However, even if persistent gratings can be written in dyed polymer films, those observed in PDLC are basically due to the liquid crystal and its strong optical anisotropy. The presence of the liquid crystal droplets produces an enhancement of the effect that leads to the optical peculiarities of the gratings. Although the grating is due to a liquid crystal orientation inside the droplets, we exclude that the effect depends from the reorientation induced by the optical field. We have made PDLC samples changing the liquid crystal component. The criteria used to choose the nematic liquid crystal were the following: comparable nematic range and optical anisotropy, and different sign of dielectric anisotropy $\Delta\varepsilon$. For this reason the nematic ZLI-4788 was chosen, having $\Delta\varepsilon$=-5.7, opposite to the value of E7 ($\Delta\varepsilon$=10). In table 3 we report the experimental results of the measured efficiencies for samples PMMA-ZLI-D2 and PMMA-ZLI-D37. Two main features are evident: no anisotropy and lowering of $\eta_P$ and $\eta_S$. These results confirm our hypothesis on the role of liquid crystal and suggest the possibility that the orientation effect be due to the presence of an internal field.

Another already mentioned characteristic is the erasure of the gratings by means a uniform irradiation from one of the two writing beams[11]. The grating is completely erased for an intensity value of $I=55W/cm^2$ and an exposure time t=20s. After the erasure an increasing of the transmitted light is observed $I_t/I_{inc}$=10%, while before the value was 0.01%. The erased grating can be rewritten, repeating this cycle many times. The diffraction efficiency for the second writing shows a 50% reduction of $\eta_P$, and this value keeps constant after successive writing.

It is well known that the most exploited peculiarity of the PDLC is the change of transmission applying an electric external field that orients the liquid crystal droplets enabling the switching between the off and on state. For this reason the behaviour of the grating under application of AC voltage has been studied. In fact, if the observed structures are due to the orientation of the liquid crystal droplets, these should be sensitive to the applied voltage. Measurements of the first diffracted beam intensity have been recorded applying a voltage above the transparency threshold value and a complete modulation of the diffracted light was observed.



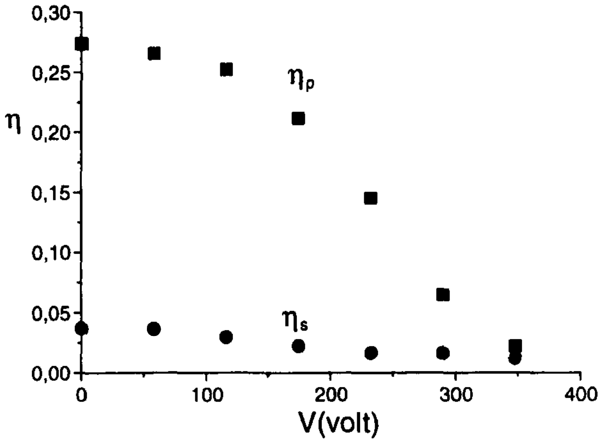



FIGURE 5 Diffraction efficiency versus the applied voltage

One result of this investigation is reported in fig.5, it show $\eta_S$ and $\eta_P$ values versus the applied voltage for PMMA-D2-E7 sample. Analogous behaviour is obtained from the different type of PDLC used[11].

In order to investigate a possible modulation in the present morphology of the material scanning electron microscopy (SEM) measurements have been made. The results of this investigation show the absence of a grating-like distribution of the droplets dimension or shape in correspondence of the optical gratings. The only difference between an irradiated region from a not irradiated one is a uniform shrinking of the droplet's size as fig.6 shows. This result can be used to explain the increased light transmission after the first writing.

TABLE 1 Efficiencies of the PDLC samples.

| | **PMMA and E7** | | | | **EPOXY RESIN and E7** | | | |
|---|---|---|---|---|---|---|---|---|
| | **D2** | | **D37** | | **D2** | | **D37** | |
| | **S** | **P** | **S** | **P** | **S** | **P** | **S** | **P** |
| $\eta_P$ (%) | 24.0 | 24.0 | 24.0 | 24.0 | 22.3 | 21.0 | 11.0 | 10.0 |
| $\eta_S$ (%) | 3.4 | 2.3 | 2.6 | 2.2 | 7.1 | 4.0 | 0.7 | 0.3 |

TABLE 2 Efficiencies of the dyed polymer samples.

| | **PMMA** | | | | **EPOXY RESIN** | | | |
|---|---|---|---|---|---|---|---|---|
| | **D2** | | **D37** | | **D2** | | **D37** | |
| | **S** | **P** | **S** | **P** | **S** | **P** | **S** | **P** |
| $\eta_S$ (%) | 0.2 | 0.02 | 0.05 | 0.05 | 0.06 | 0.06 | 0.05 | 0.05 |
| $\eta_P$ (%) | 0.02 | 0.08 | 0.05 | 0.05 | 0.07 | 0.06 | 0.05 | 0.05 |

TABLE 3 Efficiencies of the PDLC samples PMMA-ZLI-D2 and D37.

| | **PMMA** | | | |
|---|---|---|---|---|
| | **D2** | | **D37** | |
| | **S** | **P** | **S** | **P** |
| $\eta_S$ (%) | 0.3 | 0.3 | 0.2 | 0.3 |
| $\eta_P$ (%) | 0.5 | 0.4 | 0.2 | 0.4 |

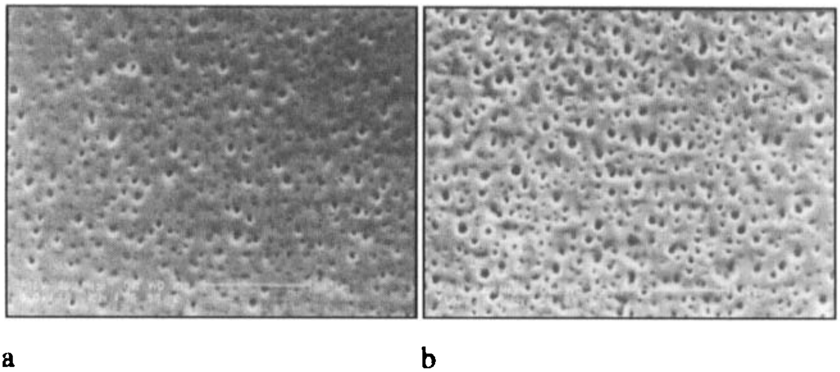



FIGURE 6 Scanning electron microscopy pictures of the grating surface. Area corresponding to the optical grating (a) and a not irradiated region (b).

## DISCUSSION

The main conclusion of the observation reported on the previous paragraph is that our gratings are essentially phase gratings due to the liquid crystal droplets. The peculiarity is the anisotropy of the diffraction efficiency for both probe polarisation beams. For phase gratings $\eta \sim (\Delta n)^2$ and the experimental results indicate that $(\Delta n_p)^2 > (\Delta n_s)^2$. This means that the induced index modulation along a direction perpendicular to the lines of interference maxima is bigger than the one along the direction parallel to these lines. The efficiency measurements suggest that the liquid crystal should be aligned inside the droplets in a direction perpendicular to the interference maxima as sketched in fig.7. This means that the s-probe polarisation would "see" a modulation of the droplet's refractive index ranging from the ordinary one $n_{od}$ to the average value $\bar{n}_d = (2n_{od} + n_{ed})/3$, giving a modulation $\Delta n_s \cong (n_{ed} - n_{od})/3$. On the other hand, the p-probe polarisation would be affected by a modulation ranging between the extraordinary index $n_{ed}$ and $n_d$, with an overall modulation $\Delta n_p \cong 2(n_{ed} - n_{od})/3 = 2\Delta n_s$. Since $\eta \sim (\Delta n)^2$ we can estimate $\eta_p \sim 4\eta_s$. Comparing this values to the results reported in the figures 2 and 3 we find that $\eta_p > 4\eta_s$, this discrepancy may be due to an amplitude grating superimposed to the phase one. If we suppose that the dichroic dye would be aligned on the same average direction of the liquid crystal inside the droplets, even if the absorption at the probe beam wavelength were quite weak, a small absorption coefficient modulation $\Delta K$ may exist.

To understand the nature of these gratings we discuss some hypothesis about the physical mechanisms that allow a permanent reorientation of the liquid crystal inside the droplets.

The first one should be a droplet's elongation due to a thermomechanical effect. The SEM investigations exclude this effect.

The second explanation takes into account the photoinduced phenomena in dye: a) photoisomerization, b) enhanced optical reorientation of the liquid crystals, c) anisotropic molecular diffusion. The observation of the storage effect in samples doped with D37 (which doesn't present photoisomerisation), exclude the point a). The point b) is dropping because the sign of the anisotropy ($\eta_p$-$\eta_s$) is independent from the writing beam's polarisation, excluding light induced molecular reorientation. The anisotropic dye diffusion was not considered since the results obtained from dyed polymer samples give no evidence of light induced dichroism, and the probe beam wavelength is far from the absorption band.

Another possible explanation concerns the orientation mechanisms of the polymer. Also in this case the effect should be dependent from the pump beams polarisation against the experimental evidence.

Although both dye and polymer are necessary to have the optical storage effect, the key role is played by the liquid crystal into the droplets.

The observations of photorefractive effect in dye[14], polymers[6,15-18], PDLC suggest that the physical mechanism producing the orientation of the liquid crystal as sketched in fig.7, should be a photorefractive-like effect.

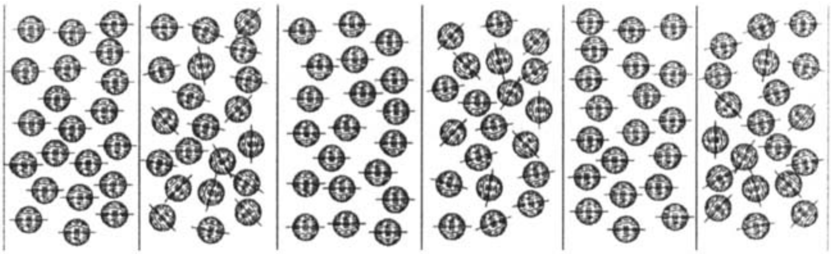


FIGURE 7 The liquid crystal droplet's orientation.

This idea is also supported by the possibility to erase the grating using a uniform irradiation. Considering this physical mechanism, a modulated stable electric field that reorients the liquid crystal director is created. All the experimental observations are consistent with this hypothesis. In particular it is supported by the experimental results obtained from permanent gratings written in PDLC with liquid crystals of different dielectric anisotropy. In fact, in this case we observe a sensitive variation of the efficiency anisotropy changing only the low frequency dielectric anisotropy of the nematic liquid crystals. These conclusions constitute the starting point of new investigations to prove the photorefractivity of the material.

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