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Anchoring Induced by Porous Substrate on a Liquid Crystal Layer

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We report the evidence of an ordered director configuration induced by a porous polymeric substrate on a thin liquid crystal film. The experiment shows that the porous substrate is able to induce a planar anchoring on the liquid crystal layer wetting its surface, while no such a phenomenon is observed if the substrate has no pores.

Keywords: *anchoring effects, porous media*

Heterogenous systems which have a liquid crystal as one of the components are attracting more and more attention by several scientists. Among them polymer dispersed liquid crystals and porous media impregnated by liquid crystals seem suitable to study interfacial phenomena since the physical properties of these materials are strongly influenced by the anchoring effects of the liquid crystal molecules on the surrounding surface. Effects of these structures on phase transitions^{1–5} linear⁶ and nonlinear optical phenomena^{7,8} originate in the guest material that has been studied.

Different kinds of porous matrices can be considered such as glasses or polymeric film. The former ones have a very complex structure due to the irregular shape of pores and to pores connection which can determine percolation of liquid crystal between pores. The latter ones have a simpler structure. Generally they are prepared irradiating a polymeric film with heavy ions⁹; in this way it is possible to create a structure of quasi-cylindrical pores which have a symmetrical distribution around the normal to the polymeric sheet. Moreover interconnection between pores should be absent.

Several different researches can be carried out on the physical properties of a liquid crystal which impregnates such a structure. On the other hand the porous

substrate may be used to study the interfacial phenomena of a liquid crystal lying on a not uniform surface (island surface).

In this letter we report the study of optical properties of a polymeric porous film impregnated by a nematic liquid crystal and give the experimental demonstration that the porous substrate induces a strong planar anchoring on a thin liquid crystal layer wetting its surface.

As porous matrix we used a 10 μm thick film of polyethylene terephthalate with pores diameter $d = 225$ nm and surface pores density $n = 3.5 \cdot 10^8 \text{ cm}^{-2}$. The same polymeric film was also available without pores and was used to compare different samples and to study influence of pores on the liquid crystal properties. The liquid crystal used was E7 by BDH with positive dielectric anisotropy $\Delta\epsilon > 0$. The nematic-isotropic phase transition temperature is $T_{is} = 60.5^\circ\text{C}$. All measurements were carried out at temperature $T = 22^\circ\text{C}$ corresponding to nematic phase of E7.

Samples were prepared in two different ways. In one case the polymeric film after heating it at 50°C for 30 minutes was placed above a conductive optical glass formerly wet by a liquid crystal droplet and then it was sandwiched by a second conductive glass. In this way the liquid crystal impregnated the polymeric matrix, but a thin liquid crystal layer ($< 1 \mu\text{m}$) was present between the glass and the polymeric porous film.

A second type of samples, after the same heating procedure, were prepared by wetting the polymeric porous film with E7. The film was then pressed with filtration paper in order to remove the excess of liquid crystal from the surface. In this case the amount of it that remains on the surface is negligible compared to that confined in the pores. After this procedure the film was sandwiched between optical glasses. In both cases the conductive glasses were cleaned, but not treated by any mechanic or chemical methods to induce any preferred orientation at surface.

In both cases permeation of the polymeric film was evident since the empty film is opaque ($T \approx 15\%$) because of the strong light scattering, while the filled matrix has a transmittivity $T \approx 40\%$.

In order to compare the behavior of liquid crystal with and without pores, the studied samples were prepared using a polymeric sheet with pores present only on half side. In this way every sample had two different zones one with pores and the second without pores. Therefore a transversal displacement of the sample with respect to the impinging light beam allowed to compare easily the different behavior in the two cases, without changing any other experimental condition.

Several measurements of the dependence of optical properties on the applied voltage (1 KHz) were carried out on the samples described above: light transmittivity, light transmittivity between crossed polarizers and ellipsometric measurements of phase shift.

First of all the optical behavior of the polymeric film without liquid crystal was checked. The light transmitted between crossed polarizers showed a clear anisotropic behavior rotating the sample around the normal to the film plane. The anisotropy axes (probably induced by stretching) has the same orientation in the film with pores as in the film without pores thus showing a symmetric distribution of pores around the film normal (Figure 1).

We will report elsewhere a detailed account of all the measurements performed

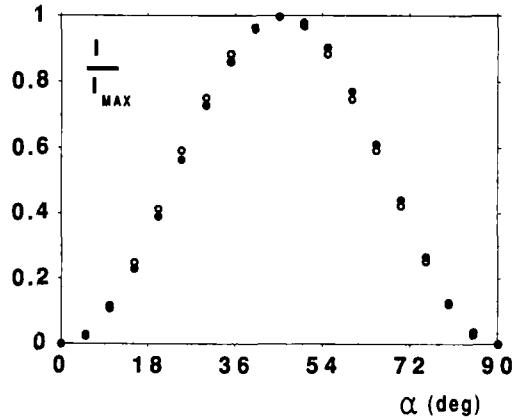


FIGURE 1 Transmitted signal when the sample is rotated between crossed polarizers. $\alpha = 0^\circ$ and $\alpha = 90^\circ$ correspond to the positions of the eigenaxis. White dots: polymeric film without pores; black dots: polymeric film with pores.

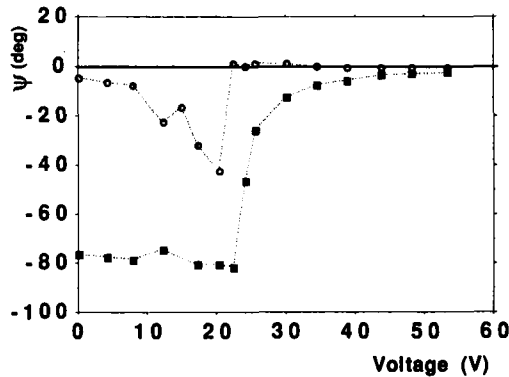


FIGURE 2 Orientation of the sample's eigenaxis versus applied voltage. $\Psi = 0$ corresponds to the orientation of the eigenaxis of the polymeric film. White dots: sample without pores; black dots: sample with pores.

on samples impregnated by liquid crystal since we want to show here only the ones which demonstrate the anchoring effect of pores.

In samples carefully prepared to remove any excess of liquid crystal above the polymeric film no variation of the optical properties was observed by increasing the applied electric field up to a value which produced breakdown of the polymer. Thus no reorientation effect occurs in samples when liquid crystal is only in the pores. This observation is in agreement with the several experimental evidence^{10,11} of a planar-radial ordering of liquid crystal inside cylindrical cavities and which produces, as consequence, a high threshold field to induce reorientation because of the small cavity diameters correspondent to our experimental conditions.

Very different are the experimental results in samples where a thin liquid crystal layer remains between the polymeric film and the optical glass.

In Figure 2 we report the rotation of one of the eigenaxis of the anisotropy ellipse vs the applied voltage. The two different curves correspond to different

sides of the same sample, with and without pores. Zero rotation corresponds to the axis direction in the empty polymeric film. These measurements were taken by detecting the light transmitted through the sample placed between crossed polarizers, with the impinging laser radiation ($\lambda = 6328 \text{ \AA}$) normal to the sample. Under this conditions a rotation of the sample around its normal shows minima and maxima of the transmitted light, where minima occur when the incoming polarization is parallel to one of the eigenaxes of the sample.

Therefore we start from a well defined anisotropic structure where the axis are the ones parallel and perpendicular to the molecular director and arrive to a quasi-isotropic structure, through a threshold effect. In this way the observed rotation of the eigenaxis can be easily understood. At $V = 0$ the axis of the whole sample is an "average" between the one of the polymeric film and the one of the planar aligned liquid crystal. By increasing the voltage the liquid crystal becomes less and less anisotropic (for normally impinging light) so that the overall sample anisotropy approaches the one of the polymeric substrate and is coincident with that at high voltages. In this situation the molecules are aligned along the field in an "almost" homeotropic configuration. Now, since the only difference between the two experimental conditions is the presence of pores in the second case, we can conclude that the porous substrate gives rise to a definite anchoring in the liquid crystal layer above it, while a plane polymeric film of the same material does not. This important observation means that, as expected, the director configuration in the cavities is planar-radial, i.e., normal to the pores' axis and, most important, this "planar" alignment is transferred to the liquid crystal layer above the pores. What have been explained here on the basis of our experimental data can be confirmed by a conventional calculation on the Fréedericksz transition for a planar structure.

It is important to underline that in Figure 2 we observe the threshold at a voltage $V = 22 \text{ V}$ applied to the whole sample. This observation is in good agreement with our explanation of a Fréedericksz transition. In fact only a fraction of the measured voltage is actually applied to the liquid crystal layer since the major drop of voltage is across the polymeric film which is $10 \text{ }\mu\text{m}$ thick. Since we know from BDH data sheet the threshold for nematic E7 is $V_{th} = 1.5 \text{ V}$ it is straightforward to calculate the liquid crystal thickness which corresponds to the measured value. We get $t \sim 0.8 \text{ }\mu\text{m}$, which is in very good agreement with the value estimated from phase shift measurements, from which we got $t < 1 \text{ }\mu\text{m}$.

Of course this anchoring property of a porous substrate will depend on several geometrical parameters like diameters of pores, average distance between neighbour pores and layer thickness wetting porous substrate.

In our experiments phase shift measurements gave a maximum value for the liquid crystal layer $t < 1 \text{ }\mu\text{m}$. Since in our matrices 14% of the surface was occupied by pores, the average distance between two neighbour pores was $\sim 2.2 \text{ d}$.

In conclusion we have shown for the first time that a porous substrate of polyethylene terephthalate with porous size $d = 225 \text{ nm}$ induces a strong planar anchoring on nematic liquid crystal wetting it. A deeper insight on this effect will be given by further studies where the different geometrical parameters will be varied.

We want to underline that the reported effect is important from a fundamental point of view since it deals with liquid crystal orientation on an island structure,

which is a very important research subject at present. On the other hand the reported observation says that studying the physics of liquid crystals in pores people must be careful to eliminate any effect coming from layers above the porous substrate.

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