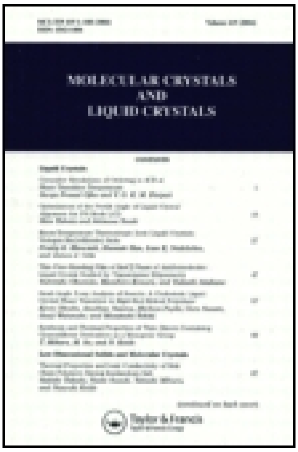

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Molecular Reorientation in PDLC Films Monitored by ^{2}H-NMR: Electric Field Induced Reorientation Mechanism and Optical Properties

R. Aloe [a] , G. Chidichimo [a] & A. Golemme [a]
[a] Dipartimento di Chimica, Universitá della Calabria, 87036, Rende, Italy

Version of record first published: 04 Oct 2006.

To cite this article: R. Aloe , G. Chidichimo & A. Golemme (1991): Molecular Reorientation in PDLC Films Monitored by ^{2}H-NMR: Electric Field Induced Reorientation Mechanism and Optical Properties, Molecular Crystals and Liquid Crystals, 203:1, 9-24

To link to this article: http://dx.doi.org/10.1080/00268949108046042

Mol. Cryst. Liq. Cryst., 1991, Vol. 203, pp. 9–24
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Molecular Reorientation in PDLC Films Monitored by ^{2}H-NMR: Electric Field Induced Reorientation Mechanism and Optical Properties

R. ALOE, G. CHIDICHIMO and A. GOLEMME
Dipartimento di Chimica, Universitá della Calabria, 87036 Rende, Italy

(Received July 26, 1990)

The molecular orientation in Polymer Dispersed Liquid Crystals (PDLC) was monitored by ^{2}H-NMR of a dissolved deuterated probe molecule in the presence of an applied electric field of variable intensity. Data of molecular orientations at different applied fields were extracted from NMR lineshapes by comparison with spectra at zero field. Such data were quantitatively analyzed using an empirical function. By comparison with optical data we concluded that the molecular reorientation due to the electric field is achieved by distortion of the minimum energy director configuration. With these highly distorted configurations the light transmission through films of the material is still low and the optical switching is in general at higher fields, when the majority of molecules are oriented along the electric field. Correlations between the reorientational switching voltage and the sharpness of the reorientation have been found and tied to the role played by different factors in orienting the liquid cristal director.

Keywords: PDLCs, field reorientation, display performance

I. INTRODUCTION

Since their introduction, Polymer Dispersed Liquid Crystals (PDLC) appeared to be extremely promising materials for their potential application in optoelectronics.[1–3] PDLC's consist of nematic microdomains dispersed within a solid, continuous, organic polymer matrix. Although it is possible to obtain nematic droplet sizes which vary within 3 or 4 orders of magnitude, only materials with domains in the 1 μm range are useful for most applicative purposes. PDLC performance is based on two typical liquid crystals properties: their birefrangence and the possibility to orient the director with external fields. In the unpowered state the nematic director orientation is determined by the interactions at the mesogen-polymer interface, modulated by elastic forces. In this state the director does not have a preferred orientation and incoming light is scattered: films of the material will then appear white to the eye. When an electric field of sufficient intensity is applied, the nematic director is oriented along a preferred direction and, if materials with the appropriate indices of refraction are chosen, the film appears transparent.

The nematic director orientation plays a fundamental role in determining the appearance of PDLC films, as above mentioned. Nevertheless, its dependence upon the intensity of an applied field is far from being understood. The structures of the nematic director in large (>5 μm) mesogenic droplets have been observed using optical microscopy[4,5] and they are in good agreement with some theoretical calculations.[6–8] Theoretical investigations of the change in structure close to the N-I phase transition have also been performed.[9,10] For droplets sizes in the submicron range structures have been experimentally studied by ^{2}H-NMR[11,12] or light attenuation.[13] NMR relaxation data also give useful information on the director structure.[14–16]

In contrast with this extensive literature existing on the director configuration in nematic droplets, not too much is known about the structural response to external fields. This is an essential point to understand for the improvement of PDLC performance but its study is not experimentally trivial. In our knowledge there is only one experimental investigation on this subject,[17] dealing with reorientation dynamics in nematic droplets. In that study both absorbance measurements in PDLC doped with a pleochroic dye and light attenuation measurements were performed and information regarding the mechanism of director reorientation were inferred.

In this paper we intend to show how detailed information on the director configuration can be obtained by ^{2}H-NMR. It has already been shown[11] how deuterium NMR lineshapes are sensitive to the director configurations in the droplets. Here we will show how this technique can be used in the presence of an applied electric field. In this case lineshapes directly reflect the molecular orientation respect to the external magnetic and electric fields. In this way, the progressive orienting effect of an electric field of increasing intensity can be followed in detail. The ^{2}H-NMR method gives results more readily interpretable respect to the light attenuation techniques and, at the same time, it gives more detailed information than the absorbance technique. The orientational informations obtained from our deuterium spectra have been interpreted in terms of an empirical model in which all factors contributing and opposing the field orientational effect are considered. Comparisons between the liquid crystal director reorientation and the light attenuation properties can then be made.

II. EXPERIMENTAL

Samples for the NMR and the light transmission experiments were made using two different techniques, depending on the materials used. In one case we had formation of droplets by polymerization induced phase separation (PIPS), where the liquid crystal is added to a mixture of two organic compounds capable of undergoing a polymerization reaction. The mixture is homogeneous at first but, as the average molecular weight of the polymer becomes higher, the liquid crystal is less and less soluble, until it phase separates as droplets which, at the end of the polymerization reaction, are trapped within a solid phase. In this way we prepared samples using Bostik A and B epoxy glue (from Bostik SpA, Italy).

A second method of preparation involves the use of a thermoplastic polymer, which is melted and mixed with a liquid crystal. The resulting homogeneous mixture is then cooled at a controlled rate and a Temperature Induced Phase Separation (TIPS) occurs if the two substances have a miscibility gap at lower temperatures. Also in this case the resulting material consists of droplets of liquid crystal within a solid polymer. Using this technique we prepared PDLC's with two kinds of polymers: Polymethylmethacrylate (PMMA, from Aldrich), and a polymer obtained from the reaction of the epoxy resin EPON 828 (from Shell Chem. Co., USA) with n-Butylamine or t-Butylamine (from Aldrich). Using PIPS, droplet sizes can be controlled changing the relative amounts of liquid crystal and polymer, as well as the temperature of curing. Using TIPS, the size is instead dependent on the cooling rate, although the relative amounts of the materials is important as well. With a faster cooling rate smaller droplets are usually obtained because the hardening of the polymer does not leave enough time to the droplets to grow.

In all cases we used the nematic eutectic liquid crystal mixture E7 (from BDH, England). The deuterated material used for ^{2}H-NMR experiment was hexamethylbenzene-d_{18} (from Cambridge Isotopes Labs., Woburn, USA). This choice is due to its high melting point, necessary for some preparation procedures, and to the fact that in its molecule there are 18 equivalent deuterium atoms, giving only one NMR signal and an acceptable signal-to-noise ratio. A small amount (1–3 wt%) of hexamethylbenzene (HMB) was added to the initial homogeneous mixture and, after the curing process, most of it was found dissolved in the liquid crystal droplets. In some case a consistent amount of HMB was left within the solid phase, as observed by NMR. This fact did not constitute a problem for our experiments, since the NMR signals from HMB dissolved in the liquid crystal and from the HMB within the solid matrix are different and recognizable.

Samples for the NMR experiments were made sandwiching homogeneous solutions of the uncured materials between two indium-tin oxide coated conducting glasses and letting the PDLC cure within such cells. The thickness of the samples was 1.00 ± 0.05 mm and it was controlled using glass spacers. NMR experiments were performed while applying a 50 Hz AC voltage of variable intensity along a direction normal to the magnetic field. Spectra were recorded on a Bruker WM 300 spectrometer, operating on deuterium at 46.05 MHz. Given the width of the spectra, of the order of 10 kHz, the quadrupolar echo technique[18] was used. Between 800 and 1000 scans were accumulated for each spectrum to obtain a good signal-to-noise ratio. All spectra were recorded at a temperature of 20 ± 1°C.

Samples consisting of thin (25–60 μm) films for transparency measurements were also made. In this case the preparation of the samples was exactly the same as for the NMR samples but a small amount of alumina spacers of the right dimensions were dissolved in the uncured mixtures. Transparency measurements were performed using a He-Ne laser as the light source and detecting the light transmitted across the films on a photodiode.

III. RESULTS AND DISCUSSION

The lineshape of ^{2}H-NMR spectra is directly linked to the director orientation respect to the external magnetic field. The resonance frequencies for a spin 1 nucleus can be written, for a uniaxial phase, as[19]:

$$\nu^{\pm} = \pm\frac{3}{4}\bar{\nu}_Q\frac{3\cos^2\theta - 1}{2} \tag{1}$$

where $\bar{\nu}_Q$ is the so called averaged quadrupole coupling constant and θ is the angle between the magnetic field and the principal axis of the averaged electric field gradient tensor at the nucleus, in our case the nematic director. The averaging of the quadrupole coupling constant is due to all the molecular motions which change the orientation of the C—D bond respect to the external field and that are fast compared to the NMR measurement time. They include conformational motions, molecular and director reorientations. In Equation 1 the Larmor frequency has been arbitrarily chosen as zero frequency. For the bulk nematic, which in our case is oriented by the external field with $\theta = 0$, we have $\nu^{\pm} = \pm 3/4\,\bar{\nu}_Q$and the spectrum will consist of two lines separated by $\Delta\nu = \pm 3/2\,\bar{\nu}_Q$. The value of $\bar{\nu}_Q$ in the confined nematic is the same as in the neat phase,[11] at least for large droplets, so that the only structure sensitive parameter in Equation 1 is the angle θ. The spectral profile can then give us a direct picture of the director configuration. Since the angle θ is spacially dependent, averaging effects due to the diffusion of the HMB probe should be considered. Nevertheless, given the relatively large spectral width, ~10 kHz, such averaging effect is not effective in our droplets, whose size is in the 1 μm range or larger. In fact, in this case the typical diffusion rate for molecules of the HMB size in nematic solvents is $\sim 10^{-7}\mathrm{cm}^2\mathrm{s}^{-1}$ and diffusion effects can be neglected.

In Figure 1 the geometrical arrangement of our NMR experiment is shown. Since for E7 both the diamagnetic and the dielectric anisotropies are positive, in this geometry the electric and magnetic fields compete to orient the nematic director. The external fields contribution to the nematic free energy can be written as[20]:

$$F = -\frac{1}{2}\int\left[\varepsilon_0\,\Delta\varepsilon\,(\mathbf{E}\cdot\mathbf{n})^2 + \frac{\Delta\chi}{\mu_0}(\mathbf{B}\cdot\mathbf{n})^2\right]dV \tag{2}$$

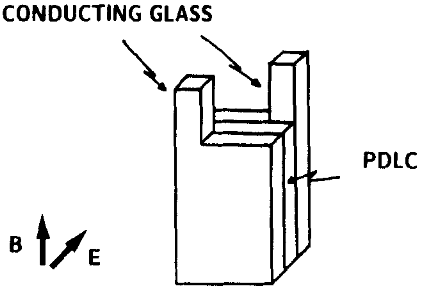

FIGURE 1 Schematic representation of the sample geometry and fields directions during NMR experiments.

where $\Delta\varepsilon$ and $\Delta\chi$ are the dielectric and diamagnetic anisotropies, respectively, and **n** is a unit vector along the nematic director. In our case the magnetic field value is fixed at 7.05 T and it can be easily shown that until our electric field is such that

$$\varepsilon_o \, \Delta\varepsilon \, E^2 < \frac{\Delta\chi}{\mu_o} B^2 \tag{3}$$

the director will be oriented along the magnetic field while it will be oriented along **E** in the opposite case. For

$$\varepsilon_o \, \Delta\varepsilon \, E^2 = \frac{\Delta\chi}{\mu_o} B^2 \tag{4}$$

all directions in the **E B** plane are degenerate.

^{2}H-NMR spectra of HMB-d_{18} dissolved in the bulk E7 at different applied fields are shown in Figure 2. In this case, where the surface effects are negligible, the switching from the orientation along **B** to the orientation along **E** is relatively sharp and almost all the sample changes orientation within ~0.2 V/μm. As predicted, the spectrum of Figure 2 taken for $E = 0.7$ V/μm shows a pattern typical of a cylindrical distributions of directors around **B**, i.e. this spectrum was acquired with conditions such that Equation 4 holds. It is remarkable that, considering that for E7 at room temperature $\Delta\varepsilon \sim 14$[21] and $\Delta\chi = 1.09\ 10^{-7}$ (erg G^{-2} cm^{-3}),[22] and that our magnetic field $B \sim 7\ 10^4$ G, a reorienting field E ~0.7 V/μm is just what we expect according to Equation 4. We ignore the origin of the central sharp peak present in all spectra but we think that it is associated with the small amount of HMB-d_{18} dissolved in the silicon glue used to seal the sample cell.

Lineshapes are quite different in the case of nematic droplets. Here we can distinguish, with no applied electric field, two different kinds of lineshape. The magnetic field can be strong enough to align the director configuration, which in our case is the so-called bipolar configuration,[11] along its direction, as shown in Figure 3a. In this case we observe spectra as the one shown in Figure 4 for $E = 0$, obtained from large droplets in the Bostik epoxy resin. In this spectrum the splitting is somewhat narrower than what we expect on the basis of the bulk spectra of Figure 2. This is due to the fact that the spectrum was taken after only one day from sample preparation. In fact, the N-I transition temperature of the nematic droplets is, with our materials, about 15°C lower than in the bulk, right after sample preparation. As a consequence, the order parameter, as well as the splitting, in the droplets is lower than in the bulk at the same temperature.

If instead the field is not strong enough to orient the directors, then a powder pattern is observed, as shown in Figure 5 for $E = 0$, in the case of droplets dispersed within a PMMA matrix. The reason for this different behaviour is probably connected both to a difference in droplet size and to different surface interactions, both factors opposing the orientation along the magnetic field. The spectrum of Figure 5 for $E = 0$ is a little different from the usual powder pattern of the Pake's type. In particular, the intensity of the external shoulders is in our case enhanced.

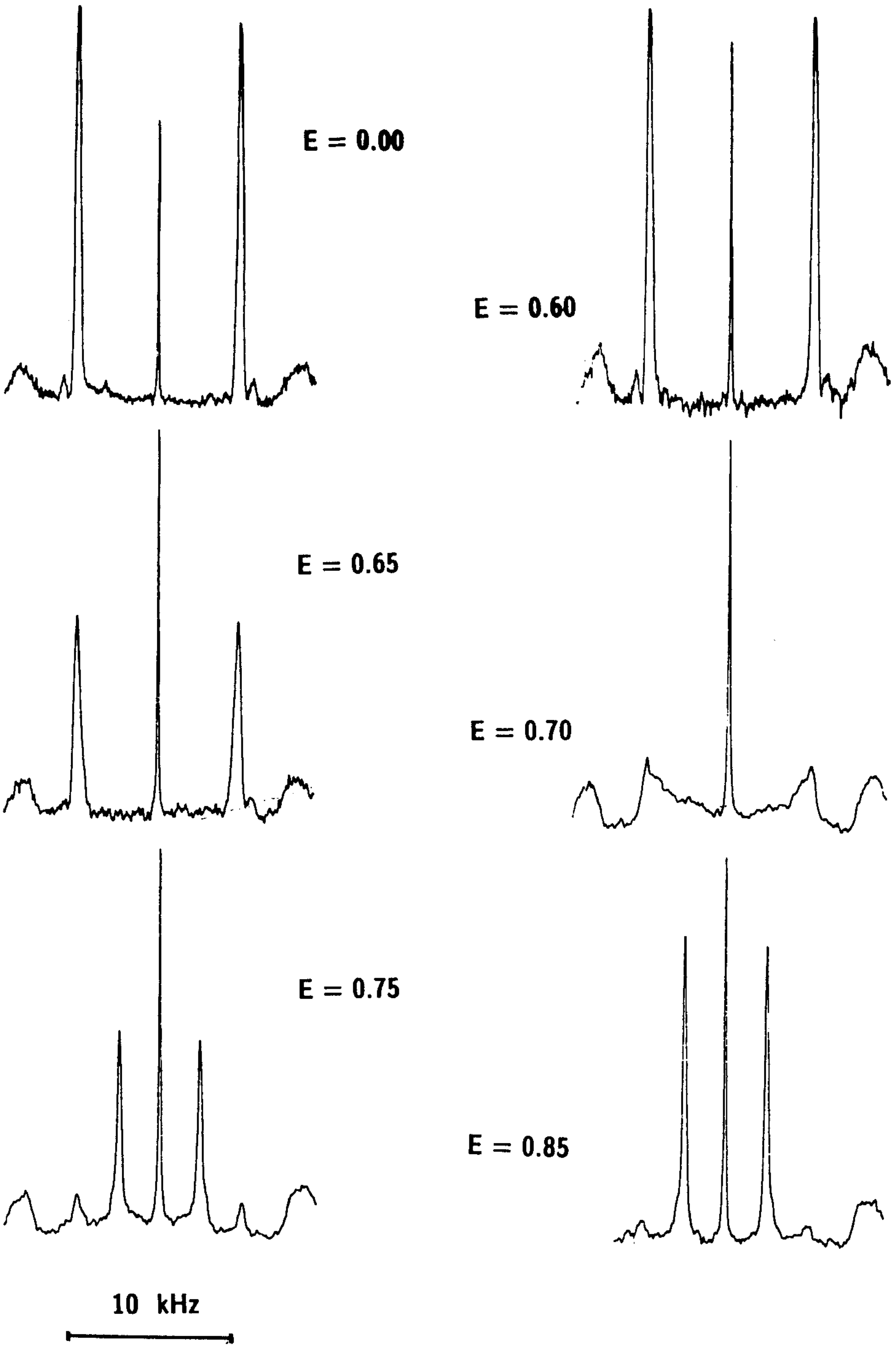

FIGURE 2 ^{2}H-NMR spectra of Hexamethylbenzene-d_{18} dissolved in the neat nematic E7 at different applied electric fields, in Volts/μm.

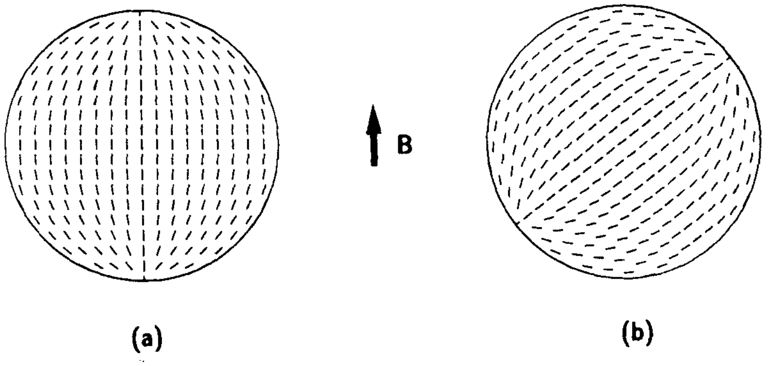

FIGURE 3 Equatorial sections, taken along the symmetry axis, of droplets in the bipolar configuration. In case (a) the symmetry axis is along the magnetic field direction.

Such distortion is probably connected with the orienting effect of the magnetic field which can distort to a certain extent the configuration illustrated in Figure 3b.

Figures 4 and 5 show two typical examples of the evolution of the ^{2}H-NMR lineshapes from HMB-d_{18} in E7 droplets as a function of the applied external field. In general, beyond a certain threshold, the intensity at the external shoulders of the patterns, corresponding to the orientation along the magnetic field ($\theta = 0$ in Equation 1), starts to decrease. At the same time the intensity increases at the center of the spectra at first, and then at the singularities, corresponding to the orientations along the electric field ($\theta = \pi/2$ in Equation 1). To obtain more quantitative information from the spectra, we need to consider a model for the calculation of the director configuration. This is not a trivial task because of the presence of two fields normal to each other, which breaks the cylindrical symmetry of the first simple models.[8] An alternative simpler procedure consists in extracting from the spectral integrals the relative amount of liquid crystal oriented by the electric field. This is done on the spectrometer computer by subtracting from the spectrum at a certain field the spectrum at zero field, both taken with the same integral. The integral of the positive part of such difference can then be divided by the total spectral intensity. In this way we obtain the percentage of molecules that are distorted from their equilibrium orientation by the electric field. Although this procedure constitutes only a rough approximation to the calculation of the director structure, it is useful since it can yield a first quantitative evaluation of this important factor. Figure 6 shows, for the neat E7 and for several PDLC samples, the percentage of liquid crystal whose director has been distorted from its equilibrium orientation by a given electric field, calculated from NMR spectra as described. These data show that the different behaviour of samples can be tied to two main parameters: the value of the electric field at which the configuration changes and the field range for a complete reorientation along **E**. The reasons for such differences are not known in detail, although several hypotheses can be drawn. The widening of the voltage range for a complete reorientation could be due to a spread in the size of the droplets. The same effect could also be explained by the existence of a different "effective" field on the liquid crystal in samples with different die-

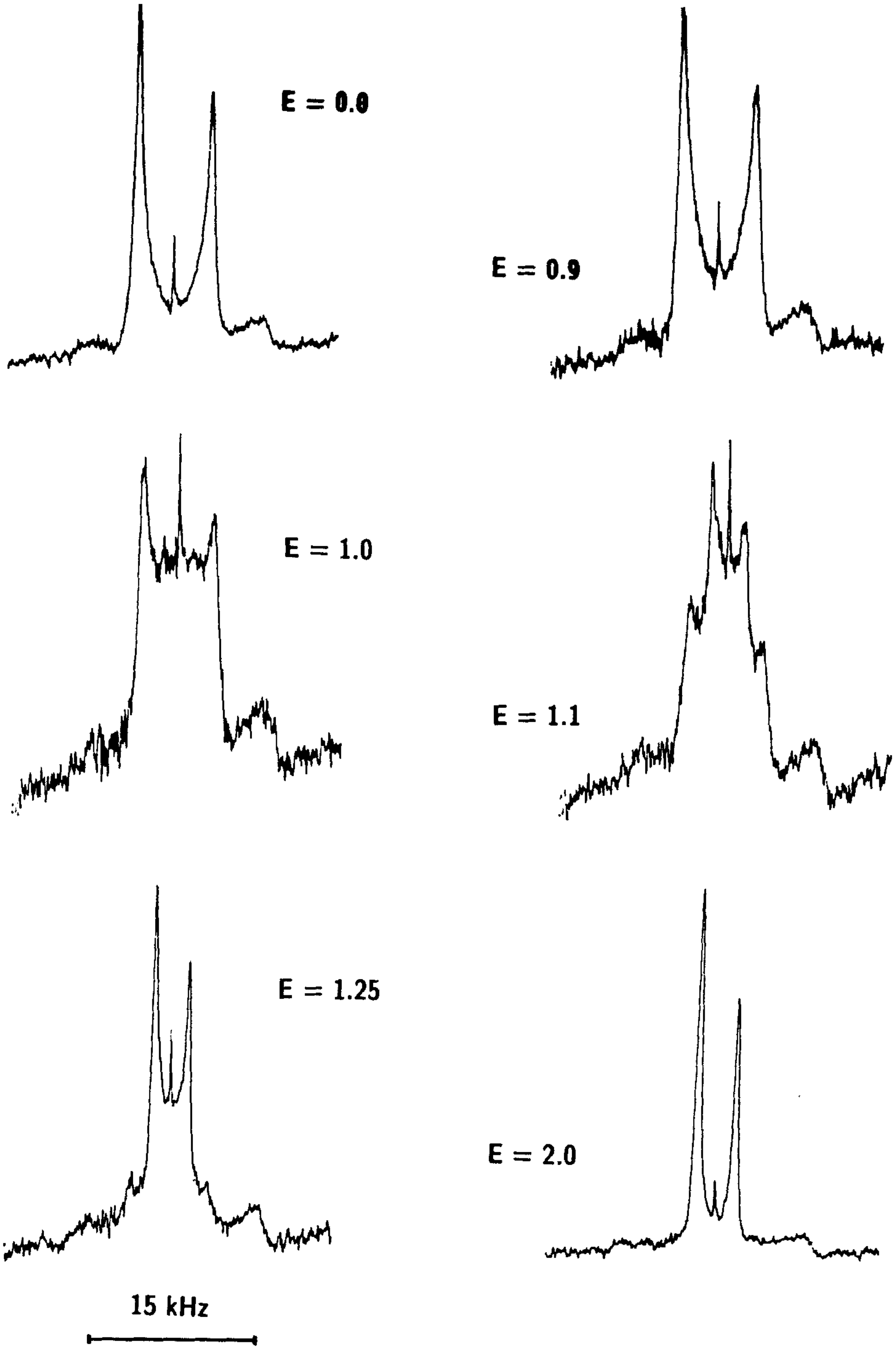

FIGURE 4 ^{2}H-NMR spectra from Hexamethylbenzene-d_{18} dissolved in E7 (33%) droplets within a Bostik matrix, as a function of the applied electric field, in Volts/μm.

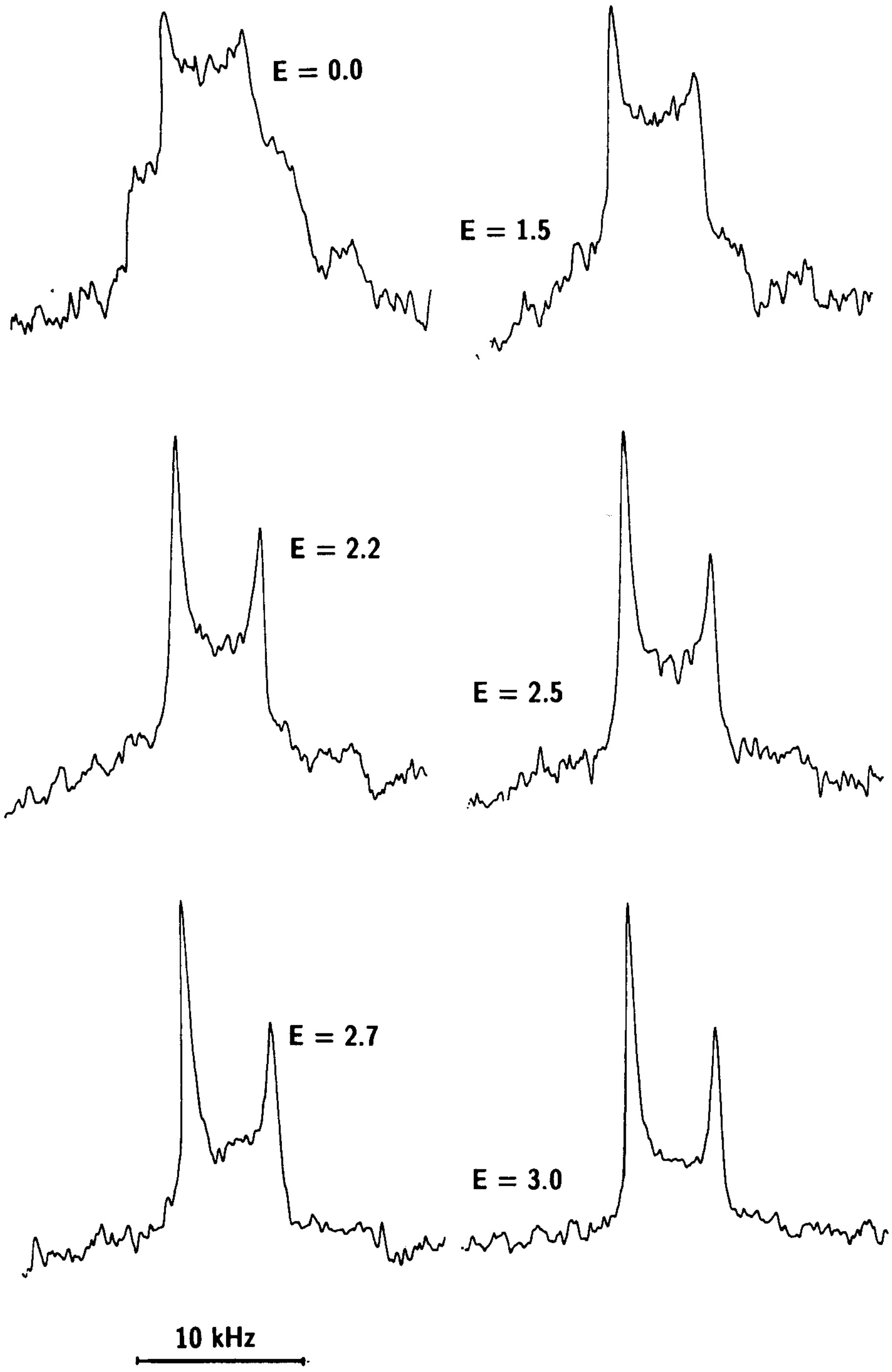

FIGURE 5 ^{2}H-NMR spectra from Hexamethylbenzene-d_{18} dissolved in E7 droplets within a PMMA matrix (sample P 0.6 in Table I), as a function of the applied electric field, in Volts/μm.

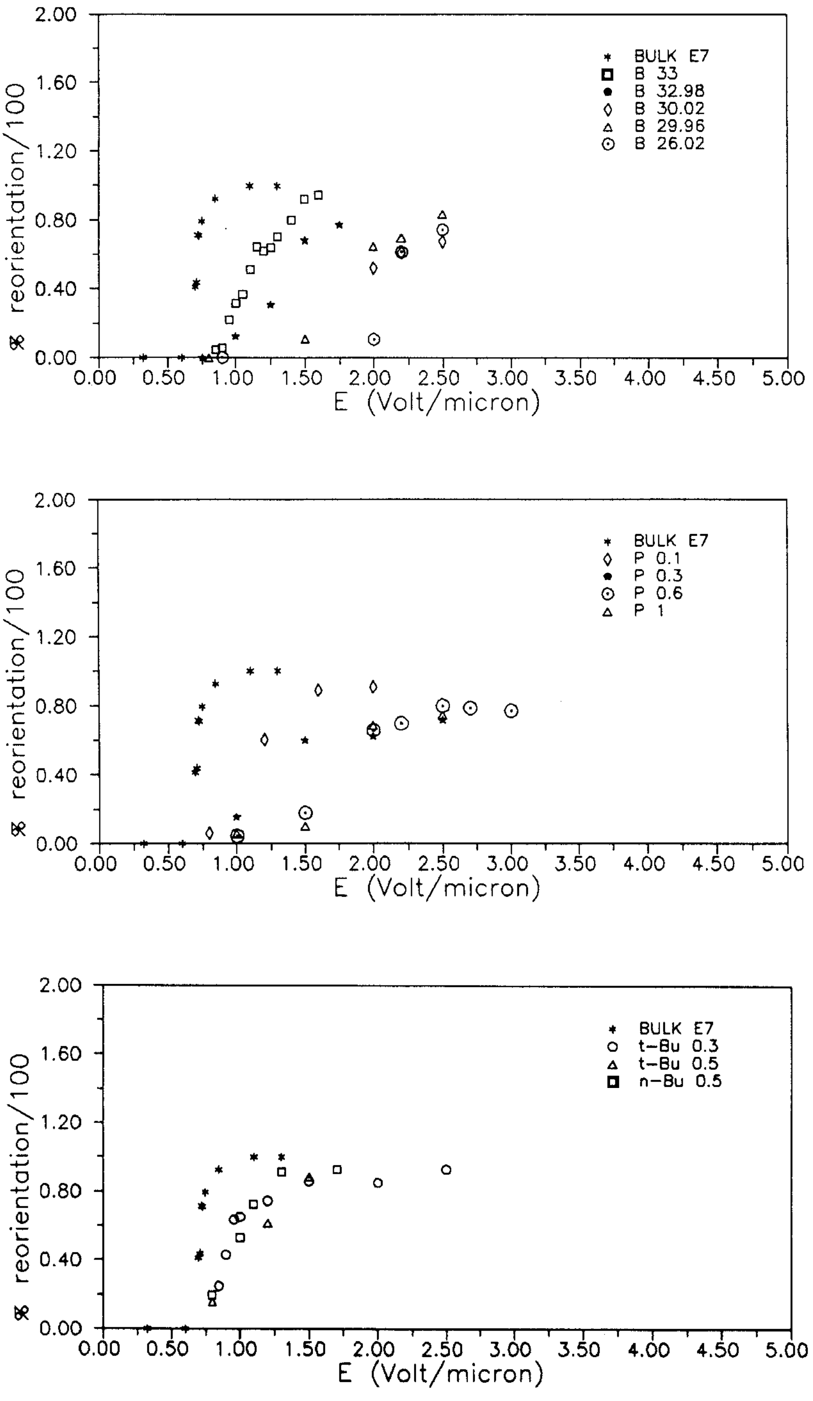

FIGURE 6 Fraction of the liquid crystal distorted by the electric field, calculated from the ^{2}H-NMR spectra of the dissolved Hexamethylbenzene-d_{18} as described in the text. Sample names are explained in Table I.

lectric properties.[23,24] The same two reasons could equally well explain the differences in the switching voltage itself.

With the aim to understand how molecular orientation is tied to the optical properties of PDLC we performed on our samples measurements of transparency at different applied fields, using the simple apparatus described in the experimental section. Results are shown in Figure 7, where 0% transmission is the transmission with no applied field and 100% transmission corresponds to the maximum transparency of the film.

To better understand the meaning of our data we attempted a fit of both the

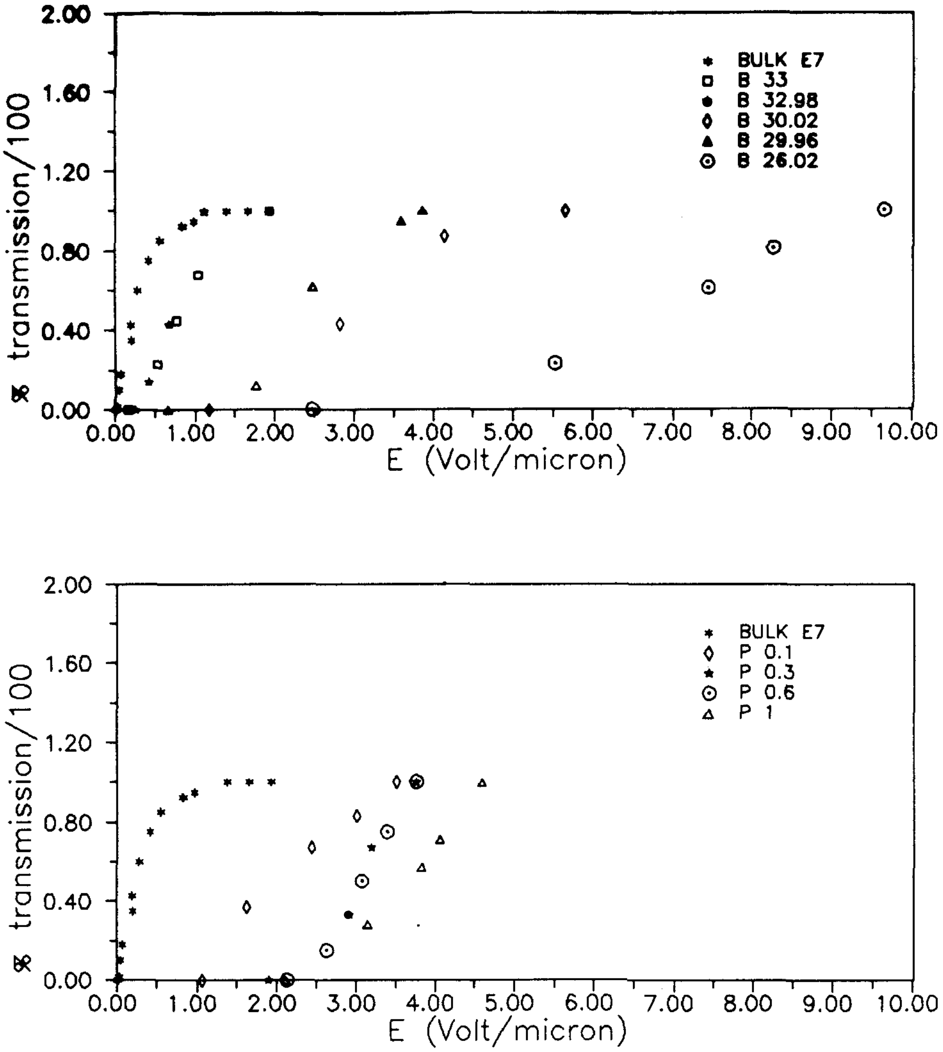

FIGURE 7 Percent light transmission through PDLC films at different applied fields. 0% corresponds to the light transmission with no applied field and 100% to the maximum light transmission. For sample names see Table I.

NMR and the optical data, shown in Figures 6 and 7, respectively, using an empirical function of the form:

$$f(E) = \frac{1}{1 + \mathrm{EXP}\left[\dfrac{-\alpha E + \gamma}{\beta}\right]} \tag{5}$$

In this function the parameter α, which can vary between 0 and 1, describes the shift of the director reorientation, or of the increase in light transmission, towards higher fields. For the bulk nematic $\alpha = 1$. A low α value corresponds to a higher switching voltage. The parameter β is instead connected with the sharpness of the rise of $f(E)$. The factor γ is necessary for comparison with the neat nematic. It corresponds, in the case of NMR data, to the field for which Equation 4 holds in the bulk nematic. In both cases it is obtained by the fitting of the neat nematic data with $\alpha = 1$. In this sense we can say that γ is measured in units of Volts/μm and α must be dimensionless, representing just a factor of field reduction. The factor β must then also have dimensions of Volts/μm and it is connected with the field range width of the reorientation process. In Table I we show the values of α, β and γ resulting from the fitting of the data shown in Figures 6 and 7 using Equation 5. Typical fittings are shown in Figure 8. It should be underlined that, since γ is obtained from the bulk data only, the parameters really varied to fit the data are just two, namely α and β.

From the α data shown in Table I we can immediately notice that the values obtained from NMR spectra are always higher than the ones from the transparency measurements. The two sets of data reflect two different physical processes. The NMR α is directly tied to the rearrangements of molecular orientations within the droplet. The transparency α is instead tied to the light transmission properties of the films which depend on the liquid crystal director orientation and many other factors.[13] The fact that $\alpha_n > \alpha_o$, where the n and o subscripts refer to NMR and optical fittings, respectively, is a direct consequence of our method. In fact, from NMR spectra we obtain the percentage of molecules distorted by **E** from their position at zero field but we can clearly see from the lineshapes that such molecules are not yet oriented along the electric field. What it must happen when we increase the electric field is then that the director configuration is distorted but the new configuration is also highly scattering. It is then reasonable to associate the rise in transparency with the "last" reorientations of the molecules in the droplets. If the molecules at the surface were the ones to be first distorted, there would be no reason for the molecules in the center not to follow them. We can then conclude that the molecules near the droplets surface require higher fields to be oriented and that the first effect of an applied electric field is to distort the configuration reorienting mainly those molecules in the center of the droplets. The reason for such behaviour could equally well be tied either to the anchoring of molecules at the surface or to the presence of a lower effective field near the droplet surface as a consequence of the dielectric properties of the materials.[24]

Another important feature of our data can be extracted looking at Figure 6. We can see that if the switching voltage is higher, i.e. if α is lower, the change in the

TABLE I

Values of the parameters obtained from the fitting of optical (right columns) and NMR (left columns) data using Equation 5

SAMPLE	α		β		$\alpha/4\beta$	
	NMR ($\gamma = 0.70$) / OPTICAL ($\gamma = 0.25$)					
BULK E7	1.0	1.0	0.050	0.11	5.0	2.3
B 33	0.62	0.30	0.078	0.06	2.0	1.2
B 32.98	0.50	0.39	0.10	0.04	1.2	2.0
B 30.02	0.35	0.085	0.15	0.05	0.56	0.42
B 29.96	0.32	0.11	0.16	0.04	0.49	0.66
B 26.02	0.36	0.037	0.12	0.041	0.75	0.22
P 1	0.35	0.07	0.12	0.025	0.73	0.7
P 0.6	0.37	0.082	0.10	0.016	0.92	1.3
P 0.3	0.46	0.083	0.20	0.018	0.57	1.2
P 0.1	0.59	0.13	0.09	0.07	1.6	0.46
n-Bu 0.5	0.72		0.095		1.9	
t-Bu 0.5	0.63		0.11		1.4	
t-Bu 0.3	0.72		0.06		3.0	

Sample names are shortened as follows: B x = Bostik and x% E7, cured at room temperature, P x = mixtures of PMMA and E7 (50%) cooled at x°C/min., *n*-Bu x = mixtures of EPON 828 and *n*-Butylamine with E7 (40%) cooled at x°C/min., *t*-Bu x = mixtures of EPON 828 and *t*-Butylamine with E7 (40%) cooled at x°C/min.

molecular orientation is less steep. Using our fitting function of Equation 5 the inclination of the curves shown in Figure 8 can be associated with the derivative of $f(E)$ at the inflection point, i.e. when $f(E) = 1/2$. It can be easily derived that the value of such derivative is $\alpha/4\beta$. In Table I we include a list of the $\alpha/4\beta$ values obtained from our fittings of the NMR and optical data. It is interesting to note how our NMR fitting parameters correlate. In Figure 9 we show a plot of α versus $\sqrt{\alpha/4\beta}$ in the case of the NMR fittings for all our samples. Considering the roughness of our method it is remarkable how, regardless of the composition, all the experimental points fall on a straight line. The same is not true for the parameters obtained from the optical data. To interpret this result we have to take into account that in our experiments we vary the electric field, the orienting energy of which is

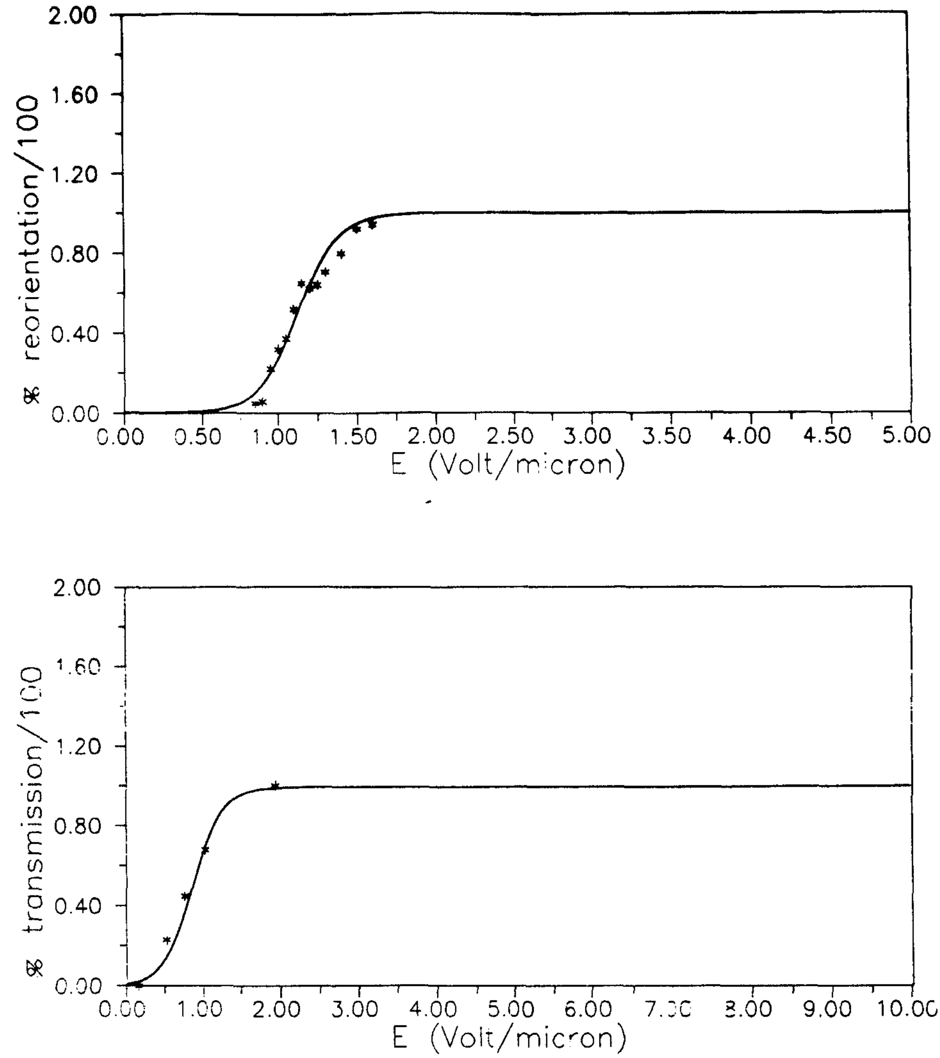

FIGURE 8 Typical fittings of the data of Figures 6 and 7 obtained using Equation 5.

proportional to the droplet volume, i.e. to R^3, where R is the droplet radius. The other factors influencing molecular orientation can be proportional to R^2, like the surface energy, or to R, as in the case of the elastic energy. This last proportionality can be easily verified in the case of the so-called star director configuration, since the elastic energy can be in this case calculated analytically.

We do not have an experimental basis for an unambiguous physical interpretation of the fact that α is proportional to $\sqrt{\alpha/4\beta}$ but we can give some reasonable explanations. In the case of $\alpha/4\beta$, i.e. when we consider the sharpness of the reorientation process, the competition for molecular orientation should be between the electric field and the elastic energy. We have already seen that this is the case

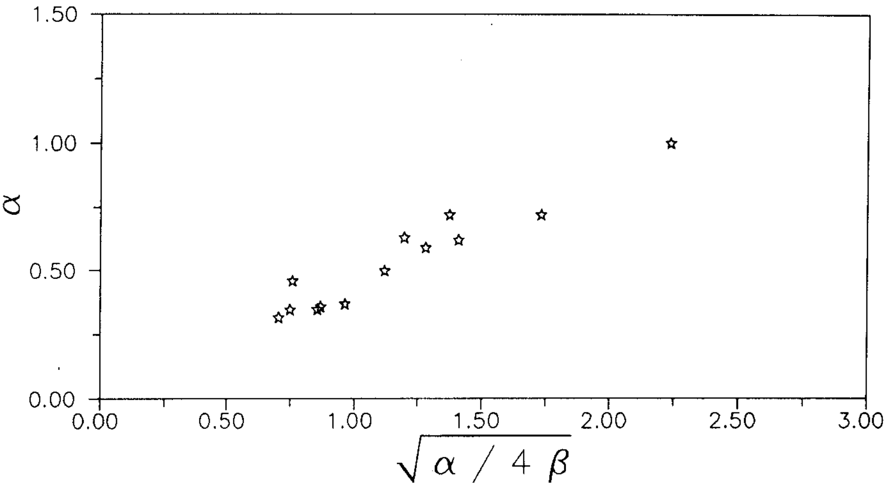

FIGURE 9 Correlation between α and $\sqrt{\alpha/4\beta}$ for molecular reorientation data extracted from NMR lineshapes.

considering the difference between the α_n and α_o and how the reorientation is associated with a distortion of the director configuration. In this case $\alpha/4\beta$ should be proportional to $R^3/R = R^2$. Given the correlation shown in Figure 9, the parameter α_n should then be proportional to $\sqrt{R^2} = R$. Since in our model α_n is a measure of the field necessary to start reorientation, this means that, in the process of molecular reorientation along **E**, the electric field competes against an energy component that has an R^2 dependence. This could be the surface anchoring energy but the effect could equally well be tied to a reduction of the effective field near the droplet surface.[24] The correlation between α and β, or better between α and $\sqrt{\alpha/4\beta}$, can then be connected to a dependence of both factors on the droplet dimensions.

IV. CONCLUSIONS

We showed that the molecular orientation in PDLC's can be monitored by ^{2}H-NMR also in the presence of an electric field. The comparison between NMR and optical data indicated that the optical switching voltage does not correspond to the voltage at which molecules start reorienting. This suggests that the reorientation develops via highly distorted director configurations where molecules at the droplet boundaries are less affected by the applied field. A correlation between the field intensity necessary for molecular reorientation and its sharpness has been observed. It confirms that the sharpness of the transition is determined by the competition between the orienting effects of the electric field and of the elastic energy. The value of the field necessary for reorientation is instead determined by the competition of the electric field with a surface phenomenon associated either with molecular anchoring or with a reduction of the effective field at the droplet boundaries. Measurements of molecular reorientation by applied electric fields of various frequencies are in progress.

References

1. J. L. Fergason, 1984, USA Patent No. 4,435,047.
2. P. S. Drzaic, *J. Appl. Phys.*, **60**, 2142 (1986).
3. J. W. Doane, N. A. Vaz, B.-G. Wu and S. Žumer, *Appl. Phys. Lett.*, **48**, 269 (1986).
4. S. Candau, P. Le Roy and F. Debeauvais, *Mol. Cryst. Liq. Cryst.*, **23**, 283 (1973).
5. G. E. Volovik and O. D. Lavrentovich, *Zh. Eksp. Teor. Fiz.*, **85**, 1997 (1983). [*Sov. Phys.-JETP*, **58**, 1159 (1983)].
6. E. Dubois-Violette and O. Parodi, *J. Physique*, **C4**, **30**, 57 (1969).
7. R. D. Williams, *J. Phys.*, A, **19**, 3211 (1986).
8. S. Žumer and J. W. Doane, *Phys. Rev.*, A, **34**, 3373 (1986).
9. D. W. Allender and S. Žumer, *Bull. Am. Chem. Soc.*, **31**, 691 (1986).
10. I. Vilfan, M. Vilfan and S. Žumer, *Phys. Rev.*, A, **40**, 4724 (1989).
11. A. Golemme, S. Žumer, J. W. Doane and M. E. Neubert, *Phys. Rev.*, A, **37**, 559 (1988).
12. A. Golemme, S. Žumer, D. W. Allender and J. W. Doane, *Phys. Rev. Lett.*, **61**, 2937 (1988).
13. S. Žumer, A. Golemme and J. W. Doane, *J. Opt. Soc. Am.*, A, **6**, 403 (1989).
14. M. Vilfan, V. Rutar, S. Žumer, G. Lahajnar, R. Blinc, J. W. Doane and A. Golemme, *J. Chem. Phys.*, **89**, 597 (1988).
15. S. Žumer, M. Vilfan and I. Vilfan, *Liq. Cryst.*, **3**, 947 (1988).
16. S. Žumer, S. Kralj and M. Vilfan, *J. Chem. Phys.*, **91**, 644 (1989).
17. P. S. Drzaic, *Liq. Cryst.*, **3**, 1543 (1988).
18. J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic and T. P. Higgs, *Chem. Phys. Lett.*, **42**, 390 (1976).
19. A. Abragam, "The Principles of Nuclear Magnetism", Oxford U. Press, London, 1961.
20. P. G. de Gennes, "The Physics of Liquid Crystals", Oxford U. Press, London, 1974.
21. E. P. Raynes, R. J. A. Tough and K. A. Davies, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 63 (1979).
22. S. T. Wu, *J. Appl. Phys.*, **58**, 1419 (1985).
23. G. Chidichimo, G. Arabia, A. Golemme and J. W. Doane, *Liq. Cryst.*, **5**, 1443 (1989).
24. P. Bucci, G. Chidichimo, A. Golemme and C. Bucci, Proceedings of the XIII International Liquid Crystal Conference, Vancouver, Canada 1990.