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Switching behavior and electro-optical properties of liquid crystals in nematic gels

P. Gautier,[1,2] M. Brunet,[1] J. Grupp,[2] J. L. Sauvajol,[1] and E. Anglaret[1]
[1]*Groupe de Dynamique des Phases Condensées, UMR CNRS 5581, Université Montpellier II, Montpellier, France*
[2]*ASULAB S.A., Rue des Sors, Marin, Switzerland*

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Anisotropic nematic gels are prepared via *in situ* polymerization of diacrylate monomers in an orientated nematic liquid crystal (LC) matrix. The switching behavior of the LC molecules under electric field is probed in polarized Raman spectroscopy and θ–2θ elastic light scattering experiments. The electro-optical characteristics of the gels are directly related to the electric field dependence of the fraction of switched molecules. The electro-optical contrast relates to the coexistence of switched LC domains and LC domains anchored to the polymer network.

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The orientation of liquid crystals (LC's) at interfaces and in confined geometries is a topic of current interest [1]. Anisotropic nematic gels can be prepared via UV photoinduced polymerization of diacrylate monomers within a nonreactive nematic liquid crystal matrix oriented by planar and uniform anchoring on the substrate [2]. This leads to an anisotropic polymer network oriented along the LC director, which reciprocally aligns the LC molecules. The small amount of polymer network (a few percent) induces drastic changes in the behavior of the LC under electric field. A progressive transition is obtained between the ''*off*'' transparent state and the ''*on*'' scattering state under application of an ac electric field. The structure of such composites has been extensively discussed [2–10]. The origin of the light scattering has been suggested to be related to the optical contrast between the switched LC domains and polymer-rich domains [3,7], but no direct correlation between the fraction of switched LC and the electro-optical properties has been reported yet. However, studies of the switching behavior are required both to understand the electro-optical mechanism and to improve the characteristics of the LC display devices based on this effect.

In this Brief Report, we investigate the electric field dependence of the LC orientation. We use polarized Raman scattering experiments and θ–2θ elastic light scattering to estimate the volumic fractions of anchored and switched LC domains. We evidence correlations between the electric field dependence of Raman scattering, light scattering, and light transmission. This allows us to describe accurately the electro-optical mechanism in nematic gels.

The gels were prepared using the liquid crystal E7 (a mixture of cyanobiphenyls and cyanoterphenyl, nematic between -10 and $60.5\,°\mathrm{C}$) from Merck, 0.5 to 3 mol % of a fluorinated dimethacrylate mesogen monomer (4,4′-bis[4-(6-methacryloyloxy)-hexyloxy]benzoate)-1,1′-perfluorobiphenylene, hereafter refered to as 4d, synthesized by T. Chuard and R. Deschenaux, Institut de Chimie, Université de Neuchâtel), and 0.1 wt % of photoinitiator (Irgacure 369 from Ciba-Geigy). The substrates of the cells were two parallel glass plates covered by indium tin oxide electrodes and coated with a thin film of polyimide rubbed with velvet in order to induce a uniform planar alignment of the LC molecules [11] (the direction of the LC molecules at the polyimide surface is hereafter refered to as the *aligning direction*). The cells were made with two substrates separated by 9 μm spacers and then filled at room temperature by capillarity and exposed to UV light for several hours. At the end of the reaction, about 80% of the monomers have polymerized, as determined in Fourier transform infrared measurements [12]. The light transmission of the as-prepared cells was measured as ranging between 80% and 90% (it is essentially limited by Fresnel reflections on the substrates).

The fraction of switched LC molecules can be estimated from polarized Raman scattering measurements. We studied the electric field dependence of the Raman intensity of the cyano (CN) stretching mode of the LC (there are no CN groups in the momomer or initiator), whose Raman polarizability tensor can be approximated by a diagonal matrix in the molecule (xyz) reference frame [16]. In the ''off'' state, the Raman intensities in the laboratory (XYZ) reference frame I_{ZZ} and I_{YY} are proportional to the squares of the tensor components α_{zz} and α_{yy}, where the subscripts refer to the polarization of the incident and scattered light, respectively. When the LC molecules are switched, the components of the Raman polarizability tensor in the laboratory reference frame change according to the molecule orientation. The I_{ZZ} intensity is expected to decrease significantly while the I_{YY} intensity should remain almost constant. This is sketched in Fig. 1(a) and has been checked on a cell filled with pure LC [Fig. 1(b)]. If one assumes a dual domain system where the LC molecules are either anchored to the polymer network and parallel to Z or switched and parallel to X, the measured I_{ZZ} intensity is the sum of the contributions from the anchored ϕ_a and switched ϕ_s volume fractions:

$$I_{ZZ}^{gel}(U)=\phi_s I_{ZZ}^{LC}(U)+\phi_a I_{ZZ}^{gel}(U=0), \tag{1}$$

where the superscripts *gel* and LC refer to measurements on the gel samples and pure LC sample, respectively, and $\phi_a+\phi_s=1$.

The switching behavior of the gels was also investigated in elastic light scattering experiments, using monochromatic incident radiation of wavelength $\lambda=1$ μm. The scattering intensities were corrected for Fresnel reflections and the angular dependent beam path. We used a θ–2θ setup in order to keep the scattering vector $\vec{q}(\|\vec{q}\|=4\pi\sin\theta/\lambda)$ parallel to

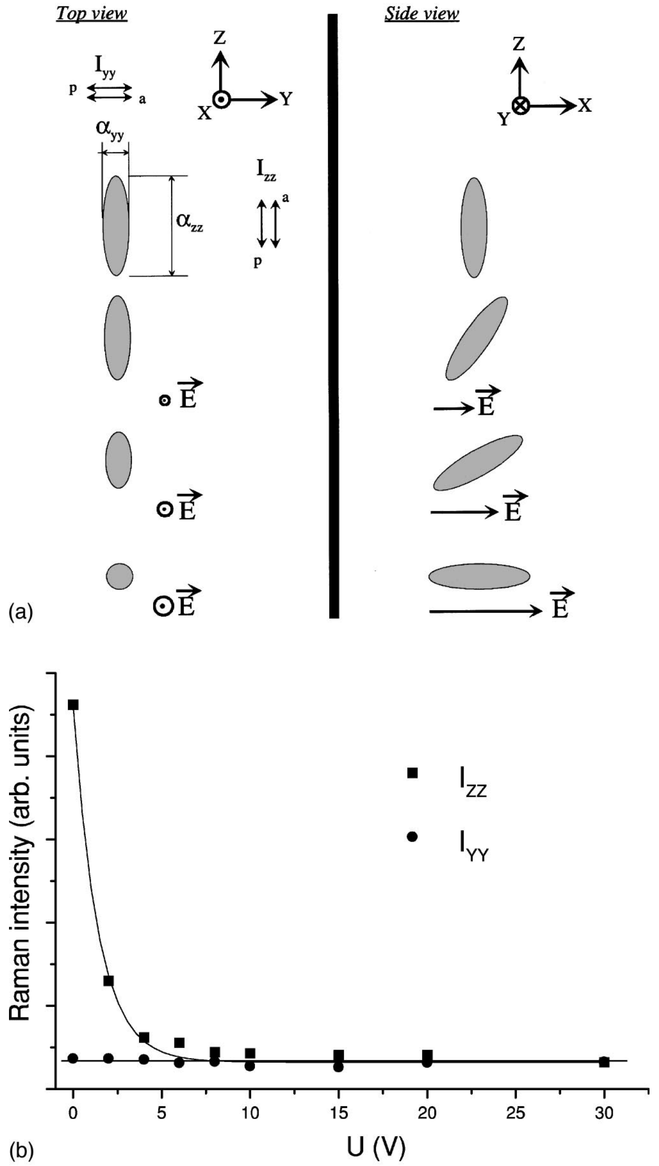

FIG. 1. (a) Sketch of the molecule switch in the molecular and Raman laboratory reference frames. $\vec{E}$ represents the applied electric field. (b) Electric field dependence of the Raman intensities I_{ZZ} and I_{YY} of the CN stretching mode for a cell filled with pure LC.

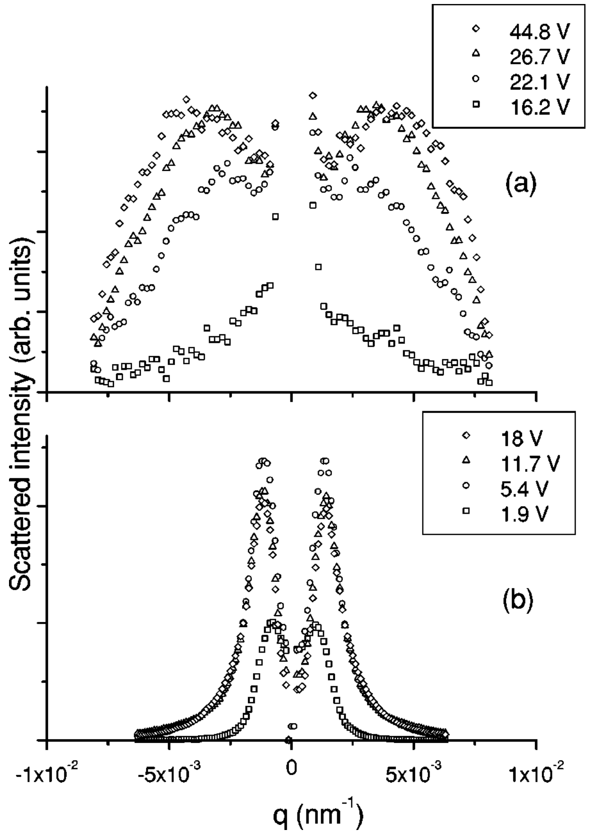

FIG. 2. θ–2θ scattered intensity in the plane perpendicular to the aligning direction for incident light of wavelength $\lambda = 1$ μm polarized parallel to the aligning direction and various electric fields: (a) 2.2–2.5 mol % 4d; (b) 0.6–0.7 mol % 4d.

the plane of the substrate and to be able to study the anisotropy of the samples. A detailed presentation of the experimental setup is given elsewhere [10]. We explored the electric field dependence of the scattered intensity for two different orientations of $\vec{q}$. For $\vec{q}$ parallel to the aligning direction [Z in Fig. 1(a)], the scattering intensity is weak and essentially independent of the electric field. It is also weak without electric field for $\vec{q}$ perpendicular to the aligning direction [Y in Fig. 1(a)] but for voltages larger than a concentration-dependent threshold an intense and broad scattering peak is measured, as already reported in Ref. [5]. Typical scattering patterns are reported in Fig. 2 for gels prepared with about 0.7 and 2.3 mol % of monomer. The location of the peak slightly but continuously shifts to larger angles for increasing voltages, while its intensity increases up to a concentration-dependent voltage and then decreases (note that for the high concentration gel the largest voltages applied almost correspond to the maximum of intensity). In the experiments presented, the incident light was unpolarized but similar profiles were measured for light polarization parallel to the aligning direction, while weak signals were measured for light polarization perpendicular to the aligning direction. Both the light polarization and scattering geometry dependences of the signal confirm the high anisotropy of the structure: essentially no polarizability fluctuation can be observed along the aligning direction, i.e., domains of polymer, anchored LC, and switched LC are aligned parallel to the aligning direction. Furthermore, the weak scattering intensity measured for light polarization perpendicular to the aligning direction indicates that there are no refractive index variations along its path, i.e., that both anchored and switched LC molecules remain essentially in the plane defined by the aligning direction and the normal to the cells. The observation of a maximum in the scattering profile indicates that there is a typical size in the system. It is not straightforward, however to estimate this typical size and to explain the electric field dependence of the maximum of the scattering peak because of the likely complex and polydisperse structure of the system. In addition, multiple scattering must be considered for large electric fields and may modify the scattering profile [13,14]. In our systems, it must be noticed that the multiple scattering contribution probably remains weak because of the small thickness of the cells. A broadening of the peak would be expected in the case of multiple scattering [14], and this was not observed experimentally. We will dis-

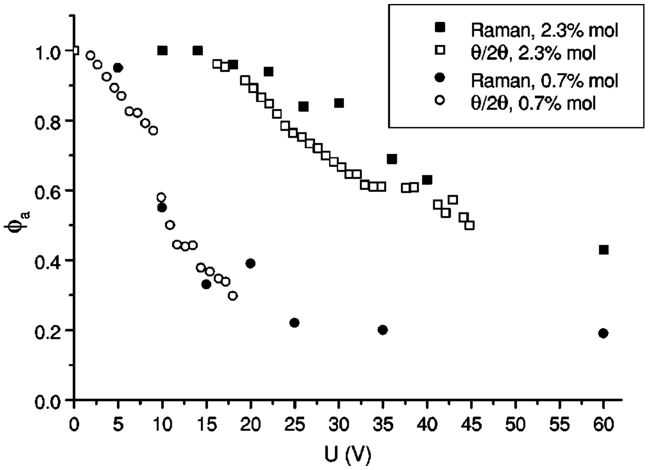

FIG. 3. Electric field dependence of the volume fraction of LC anchored to the polymer network as estimated from Raman (filled symbols) and light scattering (open symbols) measurements.

cuss possible models for the structure of the polymer networks, calculate the corresponding scattering profiles, and compare with θ–2θ data elsewhere [10]. Here, we will show that, even though the analysis of the angular dependence is not straightforward, one can easily get a picture of the scattering mechanism independently of any structural model. This can be achieved via measurement of the total energy scattered by the system, which is known to be independent of the microscopic details of the structure and insensitive to multiple scattering [15]. This is the well-known Porod invariant Q whose expression for a biphasic system is

$$Q=\Delta\tilde{\rho}\phi_1\phi_2=\int_0^\infty q^2 I(\vec{q})d\vec{q}, \tag{2}$$

where $\Delta\tilde{\rho}$ is the scattering contrast and ϕ_1 and ϕ_2 are the volume fractions of phase 1 and 2, respectively. Assuming again that the gels are dual domain systems, i.e., that the contrast occurs between anchored and switched LC domains, independently of the details of molecular orientation at the interfaces and consequently independently of the electric field, one can use Eq. (2) to estimate the fractions of anchored and switched LC as a function of the electric field (the q dependence of the scattering curves is extrapolated at large angles). Since the absolute value of the contrast is not known, each set of data was calibrated with respect to the largest value of Q measured for each sample (which corresponds to $\phi_a=\phi_s=0.5$). This allows us to estimate ϕ_a for each sample:

$$\phi_a(1-\phi_a)=Q/4Q_{max}. \tag{3}$$

The electric field dependences of ϕ_a estimated from Raman and light scattering are compared in Fig. 3. A good general agreement is found between the two techniques. The differences observed for the high concentration sample illustrate the limit of the θ–2θ technique. For this sample, the scattering peaks are large and extend up to the largest scattering angles measurable. This increases the uncertainty in the extrapolation of the q dependence at large angles and consequently that on the Porod invariant. Moreover, at the largest voltages applied, no clear evidence of a maximum of the peak intensity is observed. This occurs because $Q\simeq Q_{max}$, i.e., $\phi_a\simeq 0.5$, and this leads to a significant uncertainty in the estimation of Q_{max}. Note that one could run some measurements in an absolute scale instead of a relative one in order to avoid this latter source of uncertainty. We find for both samples a nonzero voltage threshold for switching the first LC molecules. This threshold increases when the monomer concentration increases. This indicates that the switching behavior is dominated by the polymer interface. Relations between the microstructure of the polymer network and the electro-optical properties are presented elsewhere [10]. At large voltages, a rather large fraction of LC remains anchored (between 20% and 30%). This is experimental evidence of the strong adherence of the LC molecules to the polymer network, in agreement with observations by infrared dichroism [4] and optical microscopy [3,10] that some of the nonreactive LC molecules remain ordered above the clearing temperature. It must be emphasized that this is a required condition for scattering. The results obtained for a tenuous polymer network that breaks under electric field can illustrate this point. They are displayed in Fig. 4(c) for a gel prepared with 1.5% of a nonmesogen monomer (4,4′-bis[6-(acryloyloxy)-hexyloxy]-1,1′-biphenylene, hereafter refered to as 6bab, synthesized by T. Chuard and R. Deschenaux). For this monomer, the light transmission is observed to increase irreversibly at high voltages. This is assigned to an irreversible destruction of the tenuous polymer network formed in these gels [10]. Consequently, all LC molecules behave freely and they all switch at large voltages.

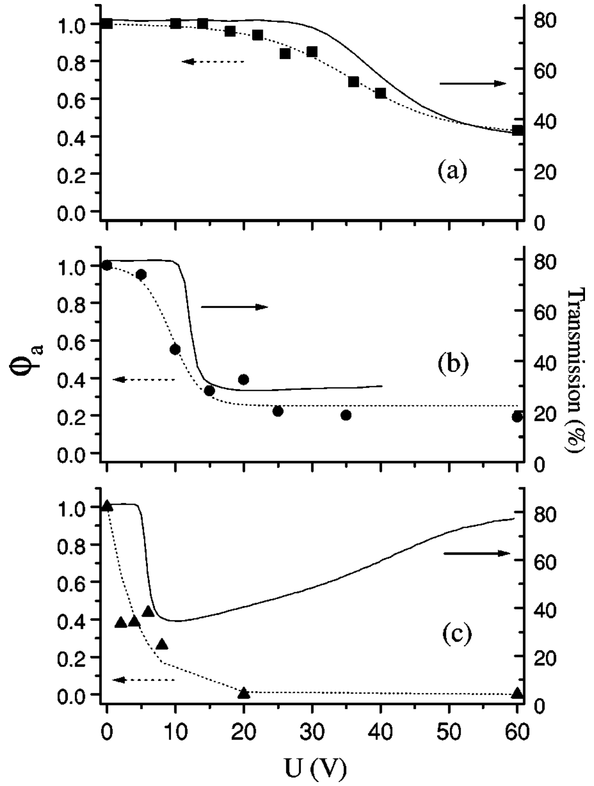

FIG. 4. Electric field dependence of ϕ_a (symbols) and light transmission (full lines) for $\lambda=0.5$ μm for gels prepared with (a) $\simeq$2.3 mol % 4d, (b) $\simeq$0.7 mol % 4d, and (c) $\simeq$1.5 mol % 6bab. Dashed lines are guides for the eyes.

Contrast is no longer available and the cells become transparent. It is also very instructive to compare this behavior with the electric field dependence of ϕ_a and light transmission measured in the visible ($\lambda = 0.5\ \mu$m) for the 4d samples (symbols and full lines in Fig. 4, respectively). They both decrease for increasing voltages in a quasireversible way. The switching threshold (Frederikzs transition) is systematically found to be larger than the switching threshold for light scattering. This is expected since a significant decrease in light transmission can be observed only if relatively large domains (of the order of the wavelength) of switched LC are grown. The relation between the amount of switched LC and the size of the domains depends on the microstructure of the samples [10] but no quantitative relation has been derived so far. By contrast, at large voltages, both ϕ_a and the transmission become constant above a second threshold voltage, and the larger the concentration of monomers the larger this threshold. This indicates as expected that the larger the concentration the larger the number of molecules interacting with the polymer network. All these results and especially the similarities between the electric field dependences of ϕ_a and the light transmission confirm that the actual scattering contrast occurs between anchored and switched domains of LC and not between the polymer and the LC, as in polymer-dispersed liquid crystals [1,17], for example. Elastic light scattering and polarized Raman scattering have been shown to be powerful tools to study the details of the switching mechanism of nematic LC's in anisotropic gels.

[1] *Liquid Crystals in Complex Geometries*, edited by G.P. Crawford and S. Zumer (Taylor and Francis, London, 1996).

[2] For a review, see R.A.M. Hikmet, *Liquid Crystals in Complex Geometries* (Ref. [1]), Chap. 3.

[3] R.A.M. Hikmet and H.M.J. Boots, Phys. Rev. E **51**, 5824 (1995).

[4] R.A.M. Hikmet and R. Howard, Phys. Rev. E **48**, 2752 (1993).

[5] R.A.M. Hikmet, J. Appl. Phys. **68**, 4410 (1990).

[6] A. Riede, S. Grande, A. Hohmuth, and W. Weissflog, Liq. Cryst. **22**, 157 (1997).

[7] G.P. Crawford, A. Scharkowski, Y.K. Fung, J.W. Doane, and S. Zumer, Phys. Rev. E **52**, 1273 (1995); S. Zumer and G.P. Crawford, *Liquid Crystals in Complex Geometries* (Ref. [1]), Chap. 4.

[8] D. Braun, G. Frick, M. Grell, M. Klimes, and J.H. Wendorff, Liq. Cryst. **11**, 929 (1992).

[9] A. Jàkli, D.R. Kim, L. Chien, and A. Saupe, J. Appl. Phys. **72**, 3161 (1992); A. Jàkli, L. Bata, K. Fodor-Csorba, L. Rosta, and L. Noirez, Liq. Cryst. **17**, 227 (1994).

[10] P. Gautier, Ph.D. thesis, Université Montpellier II, 1999 (unpublished); P. Gautier *et al.* (unpublished).

[11] J. Cognard, Mol. Cryst. Liq. Cryst. Suppl. Ser. **1**, 5 (1982).

[12] P. Gautier, M. Brunet, N. Basturk, and J. Grupp, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **321**, 383 (1998).

[13] M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation* (Academic Press, New York, 1969).

[14] J.R. Kelly and W. Wu, Liq. Cryst. **14**, 1683 (1993).

[15] T. Zemb, in *Neutron, X-Ray and Light Scattering*, edited by P. Lindner and T. Zemb (North-Holland, Amsterdam, 1991), p. 177.

[16] K. Miyano, J. Chem. Phys. **69**, 4807 (1978).

[17] G.P. Crawford and J.W. Doane, Condens. Matter News **1**, 5 (1992).