Role of Delocalized Electrons in Polyaniline−Nematogen Cyanobiphenyls Interaction

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Applying an electric field across a nematic liquid crystal display changes the texture of the thin nematic film. When the field is switched off, the texture relaxes to the initial one within seconds. Experimental evidence that very fast relaxation times could appear in some particular cases is reported. A thin film of plasma polymerized aniline induces a stronger planar anchoring of cyanobiphenyl liquid crystals. This strong anchoring appears when, due to an asymmetric conduction of the liquid crystal cell, alternating voltages create a transient electrically charged layer at the polyaniline/liquid crystal interface. This layer favors an expansion of anchoring toward the bulk, thus lowering dramatically the relaxation time and increasing the contrast ratio.

I. Introduction

Stimulated by its great economic importance the field of liquid crystals has been intensely studied, both theoretically and practically. As new experimental facts are added to the liquid crystal knowledge, the standard approach is not sufficient. Liquid crystal molecules can no longer be considered as simple rods or disks, interacting via van der Waals forces at most. To understand new and/or anomalous effects, more elaborate physicochemical theories are necessary.

In a recent paper[1] we have presented that the electric conductivity in ordered phases of pentylcyanobiphenyls (5CB) or hexylcyanobiphenyls (6CB) across phenyl rings $\sigma_\perp$ (i.e., perpendicular to the nematic director **n**) is much higher than along **n** ($\sigma_\parallel$). Typically, $\sigma_\parallel \sim 6 \times 10^{-8}$ S/m, $\sigma_\perp \sim 9 \times 10^{-7}$ S/m, leading to a relative anisotropy

$$\sigma_a \equiv \frac{\sigma_\parallel - \sigma_\perp}{(\sigma_\parallel + 2\sigma_\perp)/3} \approx -135\%$$

This large negative anisotropy has been explained by considering the contribution to the electric conduction of delocalized π electrons. This type of conduction anisotropy has also been seen and explained in the case of discotic liquid crystals.[2−5] We shall use some of the considerations presented there to understand a newly observed effect that could also lead to important practical consequences.[6]

Using the strong dielectric anisotropy of nematic liquid crystal molecules, all nematic liquid crystal displays (LCD) presently in use are based on texture changes in thin films of a nematic material under the application of a suitable external electric field, either dc or ac. The easiest way to describe the molecular alignment in a nematic layer is by the director **n**, which represents an average of the molecular long axis orientations in a very small (yet macroscopic) volume. In the absence of the electric field the equilibrium configuration of the director **n** is imposed only by the limiting surfaces. An electric field applied across this layer tends to rotate the director parallel to the field, eventually resulting a new configuration (texture) as a balance between the dielectric torque in the bulk and the restoring torques of the surfaces.[7,8] Changes in nematic textures directly influence the transmission of linearly polarized light through the film. Usually, starting with unpolarized light (for instance from a microscope bulb), a linear polarizer is placed in front of the nematic cell to create a polarized beam that traverses the cell and passes through another polarizer (analyzer) placed after the cell, having the polarizing direction at 90° with respect to the first one (i.e., crossed polarizers). In a planar cell the director in the nematic film lies everywhere in planes parallel to the surfaces (and perpendicular to the light beam). In a homogeneously oriented planar cell the director is also parallel everywhere to a plane that contains the light beam. If this plane is also parallel to one of the directions of the polarizers, the transmitted light is blocked, but it increases when rotating this plane until it is 45° to either direction of the polarizers. If the director is everywhere perpendicular to the surfaces (parallel to the light beam), the light is always blocked (homeotropic cell).

Starting with a uniform planar configuration at 45° with respect to the crossed polarizers, a strong enough electric field across the cell can induce a homeotropic texture (director perpendicular to the surfaces) that blocks the light. So, switching on and off the electric field turns off and on the transmitted light. This is the well-known Freedericksz transition (more general, the electrooptic effect).[9] It was intensely studied because it is the principal mechanism that allows functioning of LCDs. One characteristic of the Freedericksz transition in uniform planar cells is its threshold character; that is, the planar configuration does not turn to homeotropic until a certain voltage value is surpassed. Another one refers to the characteristic switch on and switch off times. Namely, when switching on the field, the strong dielectric torque turns the director to the homeotropic configuration very fast, whereas switching it off is followed by

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a relaxation of the director to the initial planar texture in a much longer time. The torque due to the anchoring properties of the surfaces normally is not so large as the dielectric torque. The characteristic time at switching the field on is the order of milliseconds, whereas that at switching the field off could be as large as seconds. In the later case, the system slowly changes the refraction index anisotropy, leading to interference fringes and the transmitted light intensity oscillates. In such a situation, the refreshing frequency of a LCD would be less than 1 Hz, truly unacceptable for nonstatic displays. To overcome these drawbacks, a strong (infinite) anchoring should be used but this, in turn, asks for larger local electric fields obtained only with thin film transistors (TFT).

We have obtained experimental evidence that very fast relaxation times appear, apparently, without very strong anchoring energies (and TFTs). Apart from their practical importance, these experiments confirm that more elaborate considerations regarding interactions within nematic liquid crystal devices are necessary to explain them.

II. Experiment

Capillary cells made out of two glass plates, ITO coated (20 $\Omega/\square$) and filled with 5CB or 6CB, were used. To avoid interpretation problems arising from the threshold character of Freedericksz transition in uniform planar cells, we have used hybrid cells. Such a cell has one plate (surface) that imposes homeotropic alignment, the other one giving planar alignment. We have observed that a bare ITO surface that had been immersed for a very short time (about 10 s) in a sulfochromic mixture (900 mL of H_2SO_4, 200 g of $K_2Cr_2O_7$, 80 mL of H_2O) gives homeotropic alignment. The planar alignment was induced by another plate coated with polymer on top of its ITO side. Different polymer films were used: polyaniline (PANI), poly-(o-anisidine), polypyrrole, and polythiophene. The films were polymerized and deposited on ITO in a plasma chamber starting from vapors of respective monomers.[10−12] The thickness of the film was measured using an ellipsometer. Although the accuracy of thickness measurement was not very high, we estimated it to be between 200 and 300 Å. The film thickness depended on the intensity and time of plasma reaction but mainly on the vapor pressure of the monomers. A simple way of changing this vapor pressure was by adjusting the temperature of the flask that contained the liquid monomer. Also, the thickness measuring technique needed the glass side opposite to ITO to be ground, making it nontransparent. The thickness of polymer films actually used in cells was only estimated from the polymerization pressure, temperature of the flasks, and time. By using appropriate Mylar spacers, the thickness of the capillary liquid crystal film was 19 μm.

As far as the plasma polymerization process is concerned, there is not yet a simple and satisfying description. What is almost sure is that plasma obtained polyaniline or other above-mentioned polymers differ in structure and properties from polymers obtained by synthetic routes.[10−12] The yellowish color of the PANI film, as well as the strong yellow color of the interior of the plasma reactor indicate that plasma obtained PANI consists mainly of leucoemeraldine base, i.e., the most reduced form;[13] see Figure 1.

Without an electric field applied, a hybrid cell configuration has a director field **n** bending continuously in a plane perpendicular to surfaces from parallel to the polymer-coated surface to perpendicular to the bare ITO surface.

If the bending plane lies at 45° to the cross polarizers directions, the light passes through the cell, although with a
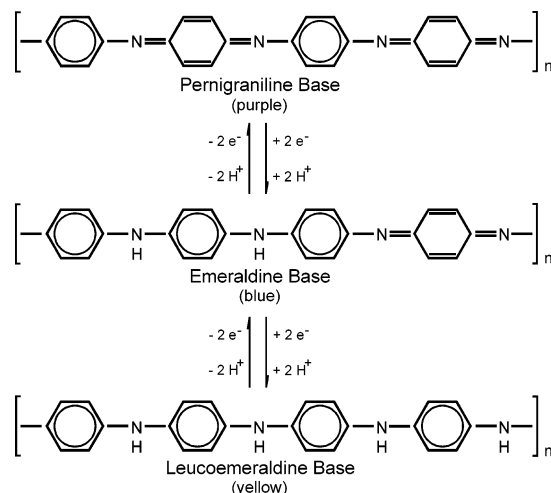

Figure 1. Three possible units of polyaniline in decreasing order of oxidation.
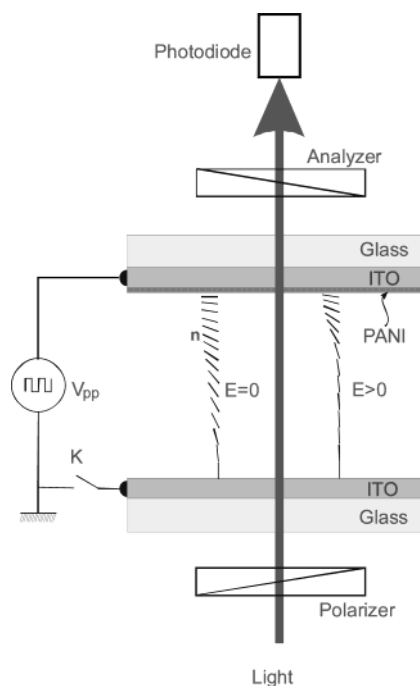

Figure 2. Sketch of the experimental setup. Polarizers and analyzers are crossed. Without applied electric field (left) there is a larger planar orientation than with an electric field (right).

transmitted intensity lower than was the case with planar cells. An applied electric field has no effect on the liquid crystal molecules already perpendicular to the bare ITO surface but forces the other molecules to align parallel to the field. The electric field increases the homeotropic character of the cell, resulting in the diminishing of the transmitted light. High enough fields succeed in overpassing the planar anchoring at PANI surface, making the cell almost homeotropic, thus blocking the light. Because on one side of the cell **n** has homeotropic orientation, in a hybrid cell the Freedericksz transition does not show any threshold voltage. Figure 2 sketches the two above-mentioned configurations.

The transmitted light has been converted to an electric current by a fast photodiode. This signal has been displayed on a CRT of a very fast digital oscilloscope and saved in digital form for subsequent processing.

On each sample several spots were individuated that provided maximum transmission light; the local director was then at 45°
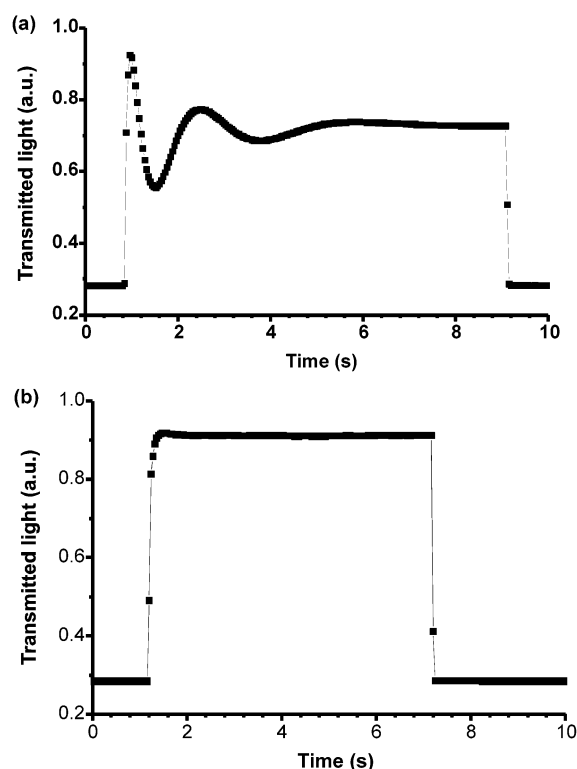
Figure 3. Transmitted light versus time. Hybrid cell, 5CB, 19 μm thick. Planar orientation with PANI, 300 Å. Phase on PANI, 80 V_{pp}, 5 kHz. Time separation between points 800 μs. (a) Switching *off* phase at instant 1 s and switching back *on* at 9 s. (b) Switching *off* ground at instant 1 s and switching it *on* at 9 s.

to the crossed polarizers. For a better alignment we have also tried rubbing but the procedure could have ruined the thin polymer film. The measurements presented in this paper were performed without rubbing.

When a strong enough voltage across the sample is switched on, the transmitted light is blocked. Switching the voltage off, the liquid crystal relaxes back to the hybrid structure with a certain characteristic time and with oscillations of the transmitted light intensity. We have used both monochromatic light (He–Ne laser, 632 nm) and "white" light (the bulb of the microscope). Although the best fringes can be seen with monochromatic light, all the records presented in this paper have been obtained using white light. From an applicative point of view, one is interested that the effects presented in the following can be obtained with white light irradiation. In Figure 3a one may see a striking difference between the switch on characteristic time (at the instant 9 s) and the switch off time (at the instant 1 s) as well as the electrooptic oscillations. (τ_{off} corresponds to the rise-up of the recorded curve and τ_{on} corresponds to the fall down of the curve).

We have found some particular experimental conditions in which this behavior is completely changed. As mentioned earlier, the electrooptic effect appears either when applying a dc voltage or an ac voltage. We have used square pulsed voltages from 50 Hz up to 15 kHz with various amplitudes from 10 to 130 V_{pp}. The voltage was provided by a function generator and amplified by a linear amplifier; both of them generated electric signals referred to a common ground, the cell itself being not grounded separately but floating. As the cell is not symmetric, there are two possibilities of applying the voltage: either the signal (phase) to the polymer coated ITO layer and the uncoated ITO layer to the ground, or vice versa. Switching the voltage off could also be done in two ways: interrupting
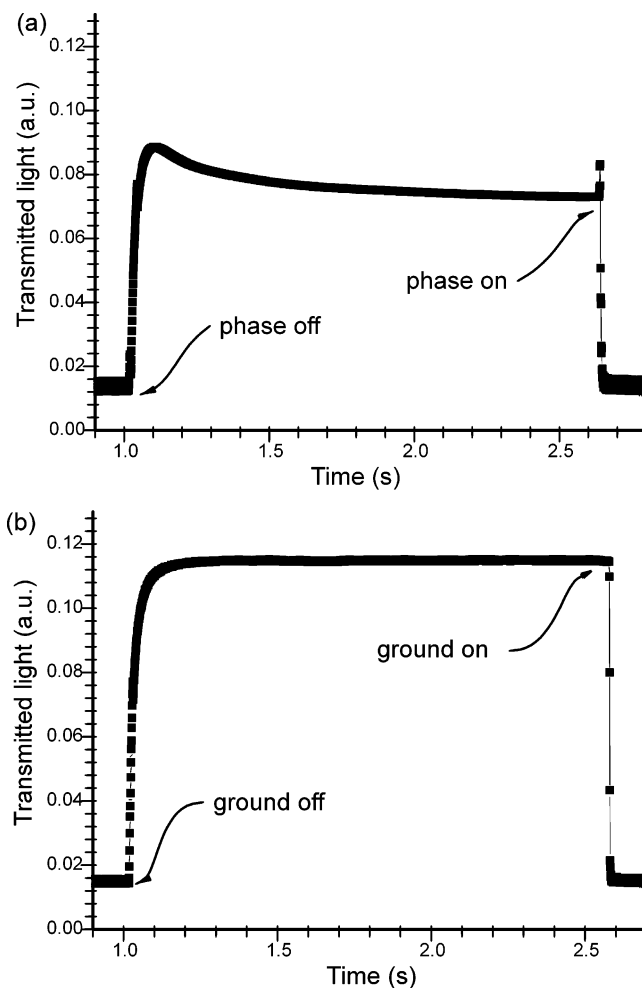

Figure 4. Transmitted light versus time. Planar cell, 5CB, 19 μm thick. Both plates PANI, 300 Å thick. Square pulsed voltage 80 V_{pp}, 5 kHz. (a) Switching phase *off* and *on*. (b) Switching ground *off* and *on*.

the phase or interrupting the ground. In Figure 3b, looking at the switch off part, one can observe the complete disappearance of the oscillations, remaining only the first rise-up characteristic of 2–3 ms, practically the same as the characteristic time at switch on. The plot also presents a higher transmission in the off state than the relaxed transmission for the standard behavior (about 1.5 times higher, comparing the amplitudes between on and off states). Of the four possibilities mentioned above, the *anomalous* effect shown in Figure 3b corresponds to the case when the phase was applied to the polymer side while the ground was switched off the other side.[6]

The anomalous effect has also been seen with symmetric planar cells that were made with two similarly polyaniline coated plates, the same thickness and the same liquid crystal. In this case there are, of course, only two possibilities: either switching off the phase or the ground. In Figure 4b, corresponding to switching off the ground, one can see an abrupt rise-up behavior, whereas in Figure 4a, corresponding to switching off the phase, one sees the oscillations. Also, in the former case the relaxed transmitted light has a higher intensity than in the later case.

Another set of experiments done with the hybrid cells consisted of first switching off the ground (attached to uncoated ITO side) and then the phase. In Figure 5a there are two plots describing the intensity of transmitted light as function of the amplitude of square pulses when the phase is on and when the phase is off (the ground being always off). With the phase off (that is, the cell completely insulated electrically) the transmitted
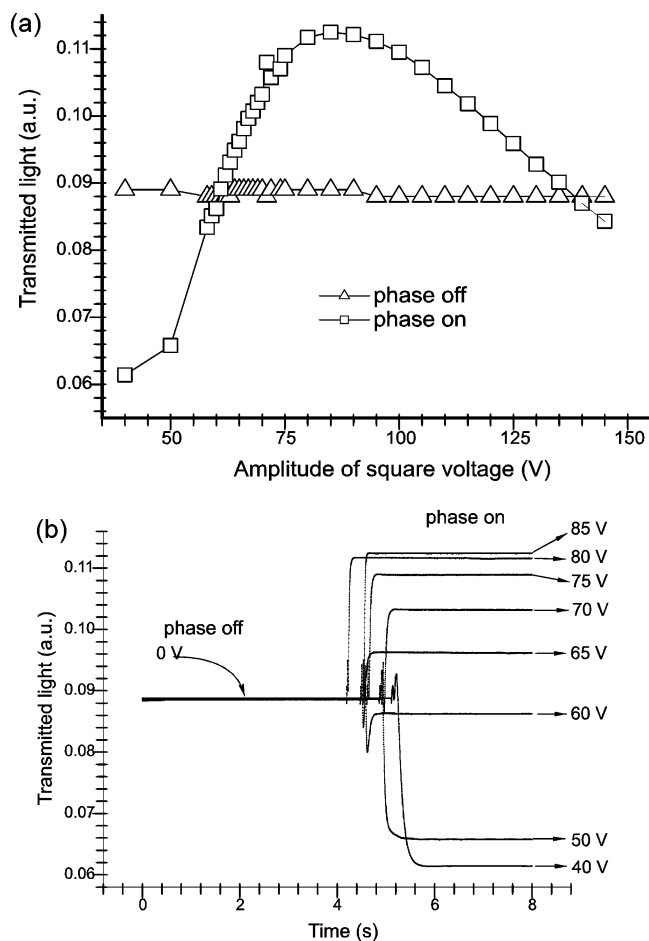
Figure 5. Hybrid cell. Phase on PANI, uncoated ITO floating. (a) Transmitted light versus voltage amplitude of phase (at 5 kHz). Triangles: phase *off* (electric insulation). Squares: Phase *on*. (b) Transmitted light versus time for different voltage amplitudes of phase.

Figure 6. Electric conduction of a hybrid cell; 5CB 19 μm, PANI 300 Å. (a) Current versus time (130 V_{pp}). (b) Current versus voltage.

light, of course, does not depend on the amplitude of the pulses. With the phase on, first at small amplitudes, the transmitted light is smaller than when the phase is off. Beyond a certain amplitude ($\sim$60 V_{pp}) the transmitted light increases and then decreases but is always higher compared to the phase off. Then, from 140 V_{pp} on, the transmitted light with phase on is slightly smaller compared to phase off. Some recorded curves are presented in Figure 5b.

It is by now clear that the anomalous effect should be linked to specific mechanisms appearing to the ITO/PANI/liquid crystal interfaces when the phase is applied to that side. No such effect has been reported with the standard polymer coating that gives planar alignment. We also checked this with good commercial cells that use polyimide for planar alignment and did not see any anomalous effect even in a wider range of frequencies or voltage amplitudes. It was normal to presume that the electronic processes at the interfaces should depend on the polarity of the signal. To check this, we have measured the steady current across the cell for both polarities of the applied voltage (the ground being always on the uncoated ITO side). In Figure 6a we plotted the current versus time for ±65 V amplitude (having applied to the sample a square wave of 6 mHz and 130 V_{pp}. It is easy to see that the conduction for negative voltage is more than twice as large as for positive voltage. Figure 6b presents a plot of saturation currents for various positive and negative voltages. Beyond a certain threshold, almost the same for positive and negative polarities, the cell presents rectifying
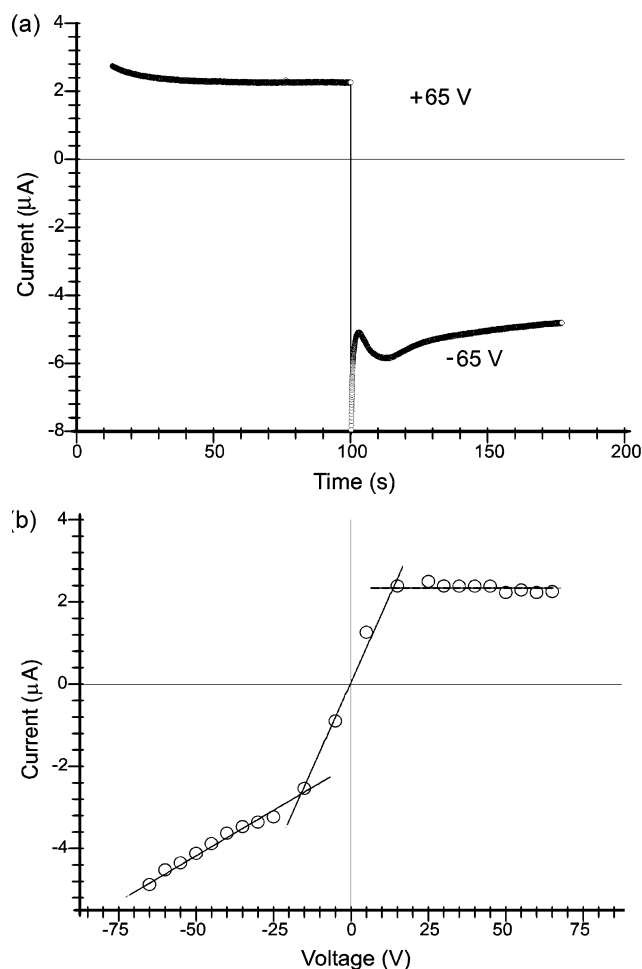
properties. The positive current is limited ($<$2.5 μA) whereas the negative current increases linearly (absolute values).

Last, but not the least, we present the measured values of the relaxation time versus voltage amplitude for several frequencies (Figure 7a) and versus frequency for several voltage amplitudes (Figure 7b). Beyond certain values, for both frequencies and voltages, the transmitted light behavior is similar to that shown in Figure 3b (even the small shoulder visible in Figure 3b disappears at larger voltage amplitudes). If the threshold values are not surpassed the behavior is similar to that shown in Figure 3a. The relaxation time was measured on a Figure 3b type curve on the rising part of it between 10% and 90% of the total amplitude. For Figure 3a type curves the 90% point was substituted with the abscissas of the first deepest minimum.

The plots in Figure 7a,b were obtained for a hybrid cell, using one PANI-coated ITO side and 19 μm thick 5CB liquid crystal layer. The PANI thickness was about 300 Å. Many other similar plots were obtained varying either the thickness of the polymer or the chemical nature of it or the liquid crystal (6CB instead of 5CB). The plots are similar but not identical; that is, the relaxation times and/or threshold values can vary from sample to sample. As far as PANI is concerned, we have observed that polymer thickness of about 300 Å gives the best (shortest) relaxation time and the smaller threshold values (for both frequency and voltage). Thinner or thicker polymer layers present poorer characteristics. Yet, the shortest relaxation time of all has been observed for a cell coated with poly(*o*-anisidine) instead of PANI ($\tau_{off} \sim$ 2 ms) but, at this stage, we cannot
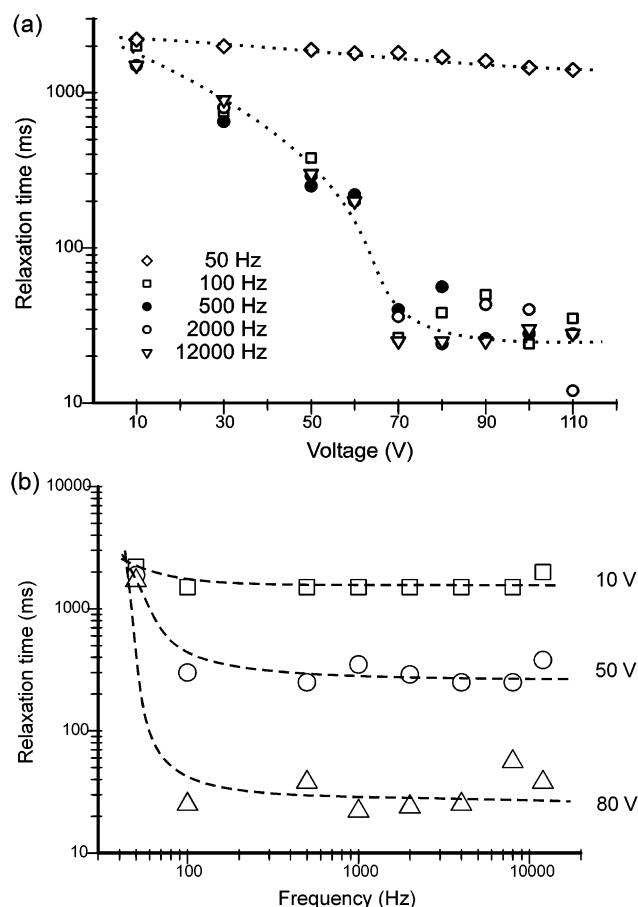
Figure 7. Hybrid cell. Relaxation times. (a) Relaxation time versus amplitude (different frequencies). (b) Relaxation time versus frequency (three voltage amplitudes).

conclude that poly(*o*-anisidine) is better than PANI; it might just happen that the thickness of poly(*o*-anisidine) and/or plasma reactor conditions concur to produce a successful result. In this respect, more systematic work remains to be done.

III. Conclusions

Let us sum up the most relevant experimental facts just presented: (i) In the first place, the anomalous effect has been observed only with PANI or polymers akin containing aromatic carbon rings. (ii) The effect appears only when the phase is applied to the polymer coated side of the cell. (iii) The simple presence of the phase on that side, even without an electric field applied within the bulk of the cell (the ground being switched off) increases the light transmission; that is, the planar alignment, within a large range of voltage amplitudes. (iv) The effect appears only with ac voltage (although most of the experiments have been performed with squared pulsed voltages, the effect can be seen also with sine voltages). (v) There are voltage and frequency thresholds. (vi) The cell has an asymmetric electric conduction, the higher current arising when the polymer side is negatively polarized.

All these facts suggest that delocalized π electrons should play an important role, as they are common both to polymers and to liquid crystals that contain phenyl rings (like 5CB or 6CB). As a matter of fact, we have also checked the effect with another liquid crystal (pentyl-5-cyclohexyl-5′-cyano-phenyl) that possesses only one aromatic ring per molecule. Although the effect can be seen, it is weaker; i.e., the relaxation times and threshold values are longer and higher. The almost planar

disposal of aromatic rings in the PANI layer contributes essentially to the planar anchoring properties of this polymer. van der Waals dispersion attraction between PANI phenyl rings and those of 5CB and 6CB strengthen this anchoring, due to the larger polarizability of π electrons. The same π electrons contribute to the electric conductivity anisotropy of these liquid crystals, as mentioned earlier in this paper.[1−5]

Let us imagine, succinctly, a mechanism that could explain the above-mentioned experimental facts. With the ITO/PANI side negative, electrons tunnel the thin ITO/PANI interface, traverse the PANI layer by fast and reversible charging of it, and enter liquid crystal reducing the aromatic rings that contain electron-withdrawing cyano groups.

Due to asymmetric current−voltage characteristic (Figure 6), one way to take advantage of the peculiar properties of the ITO/PANI/cyanobiphenyl interface is to use alternating voltage. When using ac voltage, for each negative pulse on the ITO/PANI side, electrons are injected across the polymer, forming a charge distribution. Due to diffusion in the liquid crystal (and the reservoir character of π delocalized states) and to the affinity of liquid crystal molecules to electrons, when the positive pulse is *on*, not all the electrons tunnel back trough the polymer to ITO. Therefore, on each cycle, charges accumulate at the polymer−liquid crystal interface. The accumulated charge sets in a counter-field that raises the barrier to further tunneling, on one hand, and on the other hand, some of this charge can reach the other electrode (uncoated ITO) in a time interval equal to the characteristic discharge time, RC, of the capacitor. With typical values of over 10 MΩ for R and 1 nF for C this time is about 10 ms. If the frequency of the applied voltage is higher than 100 Hz, a steady negative charge will build up in the proximity of the ITO/PANI interface. This steady charge is localized on liquid crystal molecules, increasing their polarizability and also the attractive van der Waals interaction when two neighboring molecules have aromatic rings face to face. The charge also tends to spread away from the interface to minimize the local electrostatic energy. This energy could diminish faster if the local configuration of nematic molecules is planar. The larger is the planar layer, the smaller will be the extra electrostatic energy. Both higher $\sigma_\perp$ conductivity and higher polarizability would act to increase the planar alignment. This planar alignment is, nevertheless, just a mere tendency. The electric field inside the cell has a stronger, opposite effect, eventually the cell being oriented homeotropically.

Now, switching the voltage off, the electric field disappears very fast because it is due to the charges accumulated on the two conducting ITO layers that form the capacitor. If the phase is on the polymer side, the injection of electrons continues until the negative potential of the now uniformly charged cell raises the tunneling barrier. At this time, the two contributions to higher anchoring can manifest without being counterbalanced by a strong uniform field inside the bulk.

This model is justified by the experimental facts presented above. For instance, the differences between Figure 3a,b can now be understood easily. Keeping the phase on the uncoated ITO layer and switching off the ground from the polymer side, the injection of electrons is quite small and entirely reversible. No charge accumulates at the interface. The anchoring strength is not increased, and the relaxation is slow. It also presents oscillations, the explanation of which was done many years ago considering the slow change of the refractive index leading to interference fringes.[7,8] In Figure 3b the now higher anchoring gives a shorter relaxation time, higher transmitted intensity and no oscillations. In fact, the lack of oscillations is due to the

shorter relaxation time; it is not an artifact, because the recording system (photodiode and digital oscilloscope) was set to a smaller time resolution (similar to the physiological resolution of the human eye).

Probably, the shortening of relaxation times and lack of oscillations−although very important from the application point of view−do not constitute the best evidence of the role of delocalized electrons in increasing the planar alignment. A better one is given by the experiments presented in Figure 5a,b. In these experiments we started first with the insulated cell (that is the uncoated ITO side is floating and the phase on the PANI side is switched *off*) and recorded the transmitted light. When the phase is switched *on*, the transmitted light increases, meaning that the planar alignment within the cell is better. Yet, this increase is present only when the amplitude of the square pulses lies within the range $60-140$ V_{pp}. Why only in this region? If the voltage is smaller than 60 V_{pp}, the injection of electrons through the polyaniline is small and the planar effect is also small. The charges on the ITO layer can easily follow the change of the phase polarity (even at 15 kHz) because the ITO layer has a small resistance (20 $\Omega/\square$) and small capacitance. Either for a negative or a positive pulse there will be a negative or positive superficial charge on the very thin ITO layer that creates an (alternating) electric field normal to the surface and penetrating the polymer layer into the liquid crystal. The same dielectric torque as in the case of the electrooptic effect tends to orient the liquid crystal molecules perpendicular to the surface, thus decreasing the planar order. These two competing effects are balanced at a threshold value of ∼60 V_{pp}. In fact, both the charge accumulation at the interface and the strength of the electric field in the vicinity of the ITO surface increase with the amplitude of the pulses. Whereas the electric field increases proportional to the pulse amplitude ($E = \sigma/\epsilon\epsilon_0$, and the superficial charge density σ is proportional to the amplitude $|V|$), the accumulated charge depends on the tunneling probability that increases exponentially with the amplitude (yet, only for negative pulses). We should expect the transmitted light to saturate for higher and higher voltage amplitudes. Figure 3a does not present such a behavior. This is due to the fact that a larger amount of tunneled electrons are localized on aromatic rings of molecules that are transformed into labile negative ions. When such a negatively charged ring faces a neutral parallel ring of another molecule, the attractive van der Waals interaction, both dispersion and mostly dipole induced, is larger than between two neutral rings. If, instead, the negatively charged ring faces another negatively charged ring, the now even higher van der Waals attraction is surpassed by the Coulombic repulsion between like charges. The higher is the accumulated charge at the interface, the larger is the probability that one negative molecular ion face another negative ion instead of a neutral molecule. This is another effect that hinders the planar order in the cell.

Although we do not have accurate data concerning the influence of the polymer thickness on the increase of planar order, qualitatively we have seen that very thick polymer films give a worse result. Probably this is the reason we have not seen the anomalous effect when solution cast polyaniline films are used. We have not succeeded in making a film as thin as when using plasma polymerization. Of course, the thicker is the polymer film the smaller is the tunneling probability and, therefore, the smaller is the steady accumulated charge.

Though very interesting in themselves, these effects could also lead to important technological consequences. An immediate idea consists of building pixel matrixes with one large ITO electrode covered with the appropriate polymer film on one side and an array of multiplexed pixels on the bare ITO plate. These pixels could be done in the standard way, by etching the ITO surface. All these pixels on the uncoated ITO are connected to the ground of a variable frequency voltage supply, the phase being on the polymer side. An electronic procedure can be used to interrupt the connection to the ground of each pixel, when desired.[6]

New experimental work and theoretical considerations could lead to displays operating at a higher frequency and with a better contrast ratio.

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