Dyes and Pigments 88 (2011) 1–6

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Dielectric relaxation dynamics in a dual-frequency nematic liquid crystal doped with C.I. Acid Red 2

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ARTICLE INFO

Article history:
Received 23 February 2010
Received in revised form
23 April 2010
Accepted 23 April 2010

Keywords:
Dual-frequency liquid crystals
Dye
C.I. acid red 2
Dielectric spectroscopy
Dielectric relaxation

ABSTRACT

The dielectric relaxation dynamics of a dual-frequency liquid crystal-dye composite were studied and the effect of the photoinduced isomerization of the azo dye on the dielectric spectrum of the cell under illumination by an argon-ion laser operating at wavelength of 514.5 nm and irradiance of 550 mW cm^{-2}. It was found that the illumination process has a profound influence on the dielectric spectrum of the dye-doped dual-frequency liquid crystal in the low-frequency range.

1. Introduction

Controlling liquid crystal (LC) alignment by a combination of cell surface treatment and external fields is the most common method used for all LC devices. Recently, a photoalignment technique has emerged that uses doping with azo dyes (e.g. C.I. Acid Red 2) that allows photoinduced isomerization of the dye molecules on the substrate surface to take place, by means of which, photoalignment of the LC molecules is achieved [1]. In this photoinduced *trans*-to-*cis* isomerization process, the conformation of the azo dye changes from the *trans* to the *cis* form under polarized light of a specific wavelength. The electro-optical properties of dye-doped LCs [2–7], in which the dye molecules play an essential role via diffusion and isomerization [8–11], have been investigated for many years.

Dielectric spectroscopy can be employed to study LCs doped with azo dyes. The current research group has investigated the effect of C.I. Acid Red 2 and C.I. Disperse Blue 14 on the relaxation process of doped nematic LCs using dielectric relaxation spectroscopy [12]; however, the effect of dye isomerization on the dielectric characteristics of an LC–dye composite has not been studied. This paper concerns the dielectric relaxation dynamics of a dye-doped, dual-frequency LC (DFLC), whose frequency-revertible dielectric anisotropy makes it possible for it to align either along or perpendicular to the electric field direction by varying the frequency of the driving signals. Using the continuous illumination of a laser beam to induce the photoisomerization and diffusion of the dye molecules, *real-time* observations of the frequency-dependent dielectric properties of the doped DFLC were recorded. It was found that the illumination process has a profound influence on the dielectric spectrum of the dye-doped DFLC particularly in the low-frequency range.

2. Experimental

2.1. Materials

The nematic host used in this study was MLC2048, a well-known DFLC supplied by Merck. MLC2048 possesses a positive dielectric anisotropy at low frequencies and negative dielectric anisotropy in the high-frequency region. Fig. 1 illustrates the real part $\varepsilon_{\parallel}'$ and imaginary part $\varepsilon_{\parallel}''$ of the dielectric component parallel to the measuring field of the pure DFLC at 20 °C. It shows that the relaxation frequency is about 20 kHz, where ε'' reaches to the maximum. Because the perpendicular component of the real dielectric constant is quite frequency-independent, this characteristic frequency is also

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doi:10.1016/j.dyepig.2010.04.008

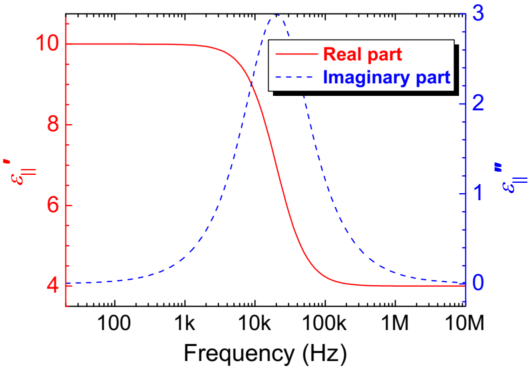

Fig. 1. Dielectric complex spectrum of MLC2048 for the parallel component $\varepsilon_{\parallel}$.

the crossover frequency, at which the dielectric anisotropy, defined as the difference between the parallel component ($\varepsilon_{\parallel}'$) and perpendicular component ($\varepsilon_{\perp}'$) of the real dielectric constant, equals zero. The relation between the crossover frequency of a DFLC and the temperature is generally given by:

$$f_c \propto \exp\left(-\frac{E_r}{k_B T}\right) \qquad (1)$$

where f_c represents the crossover frequency, E_r is the activation energy of the dielectric relaxation related to rotation around the short molecular axis, k_B stands for the Boltzmann constant, and T denotes the absolute temperature. For MLC2048, E_r is ~0.61 eV [13]. It is obvious that a DFLC, whose crossover frequency is temperature-dependent, can be utilized in thermometry. Eq. (1) implies a semi-logarithmic plot of the crossover frequency versus the temperature by assuming that E_r is independent of both T and f. It is obvious that, governed by the Arrhenius equation (see Eq. (1)), the crossover frequency is sensitive to the temperature.

The dichroic dye used as received was the azo dye C.I. Acid Red 2 (Methyl Red, MR) purchased from Aldrich. MR is known to have structural isomerism. Fig. 2(a) and (b) depicts the general structures of the MR molecule in its *trans* and *cis* forms, respectively. Note that the dichroic azo dye in the more stable *trans* form possesses a rod-like shape similar to that of the LC molecules. It absorbs the green to blue photons in the visible electromagnetic spectrum and transforms into the *cis* state.

2.2. Sample preparation

A uniform mixture of MR and MLC2048 was prepared by mechanical agitation. The concentration of MR in the solution was fixed at 0.5 wt% in this study. Due to the guest–host effect, the dye molecules were presumably aligned with the LC molecules, resulting in highly anisotropic absorption in an aligned LC cell. For dielectric measurements, cells containing the pristine LC and dye-doped LC mixture were fabricated. The electrodes of each parallel-plate capacitor used in this work were made of indium–tin oxide (ITO), and the effective area and thickness of the dielectric capacitor were 1.0 × 1.0 cm^2 and 11.0 ± 0.5 μm, respectively. In order to adapt the LC cells to laser-beam exposure for a specific experiment, each sample was confined between two transparent and electrically conducting glass substrates covered by rubbed aligning (polyimide) layers to promote uniformly planar alignment for the LC bulk.

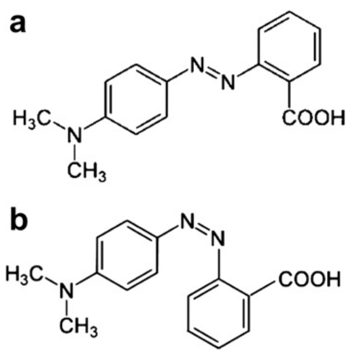

Fig. 2. Molecular structure of MR in the (a) *trans* and (b) *cis* states.

2.3. Measurements

The dielectric spectrum is the frequency-dependent complex constant expressed as $\varepsilon^* = \varepsilon' - i\varepsilon''$, where i denotes the imaginary unit $\sqrt{-1}$. We define the dielectric dispersion (or permittivity) and dielectric loss (or absorption) as the real part and imaginary part of the dielectric complex, respectively. Measurements of the dielectric spectra were carried out with a computer-controlled precision LCR meter (Agilent E4980A) having a bias voltage range ±40 V and frequency range from 20 Hz to 2 MHz. A 0.5-V$_{\text{rms}}$ sinusoidal signal was employed as the probe voltage. The sensing voltage was lower than the Frederiks transition voltage [14]. We used an effective parallel circuit to model the LC circuit and measured the capacitance and conductance with the frequency being varied by the LCR meter. The dielectric complex constant was deduced from these measured data.

To conduct the experiment of photoisomerization, an argon-ion laser (Spectra-Physics Stabilite 2017-04S) was exploited as the light source. Linearly polarized light of the 514.5-nm line, whose wavelength was close to the spectral peak of the MR absorption, was derived from the laser to permit subsequent photoisomerization of the dye molecules upon irradiation. Time-evolved dielectric characteristics were monitored for various accumulated durations of laser irradiation or in a real-time manner during the process of continuous laser illumination of 550 mW cm^{-2}.

3. Results and discussion

Fig. 3(a) and (b) shows the dielectric spectra of the respective pure and dye-doped LC cells at bias voltages of 0 and 40 V. Note that the bias voltages, 0 and 40 V, labeled in the legends correspond to the vertical and parallel dielectric components, $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$, respectively. The spectra can be roughly divided into three parts in terms of the frequency. Firstly, the low-frequency regime ($f < 1$ kHz) reveals the induced polarization due to space charge; the ionic behavior is dictated by the electrode and interface polarizations [15]. Next, the frequency range between 1 kHz and 1 MHz is related to the dielectric behavior of the LC-material system. Finally, spectra at frequencies around and over 1 MHz are dominated by the ITO effect [16,17]. Because the capacitor is non-ideal, it has a cut-off frequency determined by both the resistance and capacitance of the dielectric capacitor. In our case, the resistance and the capacitance of the cell were calculated to be 330 Ω and 80 pF in the series-circuit model, respectively, yielding the cut-off frequency of $\sim 6 \times 10^6$ Hz in the vacuum. However, the cut-off frequency can easily be altered by the dielectric constant of a medium inserted in the parallel-plate capacitor. In general, the cut-off frequency declines with increasing ε' of the dielectric material. It is clear, indeed, from Fig. 3 that the ITO "relaxation" shifts to the lower frequency (hundreds of kHz) when the real part of the dielectric constant increases (say, from $\varepsilon_{\perp}'$ to $\varepsilon_{\parallel}'$). From the 0-V data shown in Fig. 3(b), one can easily see that there is a new feature at the low-frequency range in the dielectric

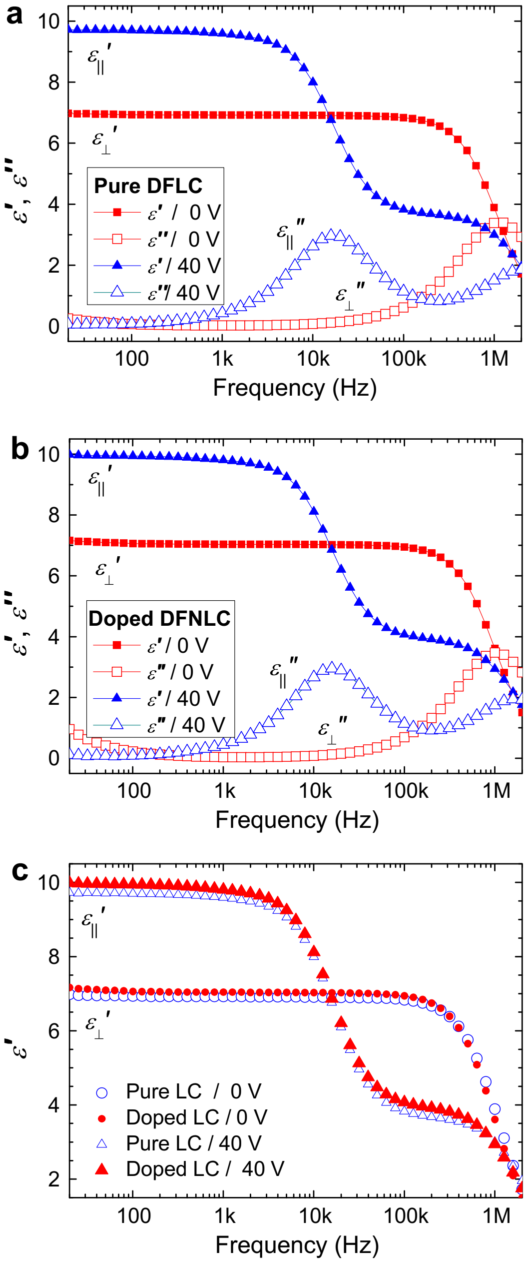

Fig. 3. Dielectric spectra of (a) a pure DFLC, (b) a DFLC doped with MR, and (c) the pristine (i.e., undoped) and MR-doped DFLC cells in comparison.

imaginary spectrum, and this is caused by superfluous ions stemming from MR doped in the DFLC. At bias 40 V, there is no dielectric loss at low frequencies for both the undoped and MR-doped MLC2048. Because of the mass ions accumulating and bound near the two substrates under the strong electric field, there is a limited amount of mobile ions dispersed in the LC bulk. The peak of the dielectric imaginary spectrum in the middle-frequency range shows the relaxation polarization of the long axis in DFLC, and this relaxation frequency is termed the crossover frequency which is the crossover point between the positive dielectric anisotropy and the negative anisotropy. Fig. 3(c) shows a comparison between the dielectric real-part spectra with data retrieved from Fig. 3(a) and (b). Fig. 3(c) suggests that the dielectric dispersion of the LC–dye composite is slightly higher than that of the pure LC system because of the volume effect of MR.

Figs. 4 and 5 display the dielectric spectra of the pure LC and the LC–dye composite for various accumulated times of laser illumination, respectively. The dielectric imaginary spectrum of the pure LC (Fig. 4) does not change apparently, indicating that the impinging light derived from the argon-ion laser has little impact on the neat DFLC system. In contrast, Fig. 5 reveals that the dielectric loss at low frequencies increases with increasing total illumination time for the MR-doped cell. This phenomenon is attributable to the MR photoisomerization from the *trans* to the *cis* state but it can be due to the contribution of ion impurities from molecular dissociation as well. The low-frequency relaxation could be associated with the dielectric double layers formed near the electrodes after irradiation as the Maxwell–Wagner relaxation is typically around 1–10 Hz. In order to examine the intrinsic relaxation polarization of the material without ambiguity, a common practice to suppress the ionic effect is to bias the sample. Fig. 6 depicts the dielectric imaginary spectra of MR-doped MLC2048 for various illumination times (0, 10, 20, 30, 40, 50 and 60 min) under bias voltage of 40 V. Note that the durations of 20, 30, 40, 50 and 60 min here correspond to a total accumulated illumination of two, three, four, five and six 10-min temporal segments with an idle time of 3 min plus a pause of ~100 s for a dielectric scan after each 10-min segment. The total break time allowed the sample to stabilize at the room temperature for each dielectric measurement. It clearly shows that, in each spectrum of the doped cell receiving a certain amount of laser exposure, there seems to exist a dielectric loss peak at a low frequency below the range of measurement. This "peak" is not related to the ion effect originating from the impurities in the LC [18] but arises apparently from the *cis* MR molecules, which together exhibit macroscopically a lower AC resistivity at low frequencies and, presumably, a higher DC conductivity compared with those of their *trans* counterparts. Noticeably, the dielectric loss tends to saturate with increasing irradiation time and reaches the saturation at about 30 min, manifesting an equilibrium between the *trans*-to-*cis* photoisomerization and the reverse transformation imposed by the ambient heat. This finding sheds light on the feasibility to measure qualitatively the level of *trans*-to-*cis* isomerization of MR molecules using the dielectric complex spectrum in the low-frequency regime. Here it is worth mentioning that a prolonged, high-intensity laser illumination may induce decomposition of an azo dye and, in turn, lead to the change in conductivity. We have ascertained that the decomposition is not an issue in this study and the doubts associated with the dye fragments and charged radicals are ruled out.

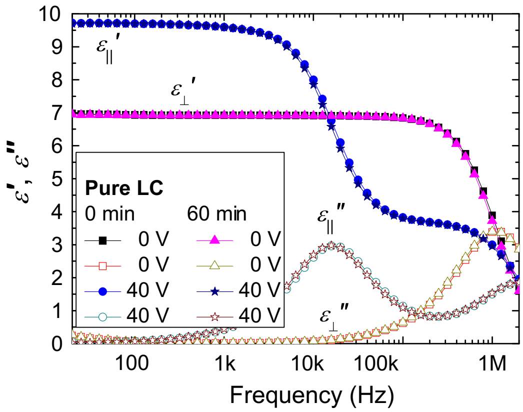

Fig. 4. Dielectric spectra of a pure DFLC cell under light illumination for 0 and 60 min (Filled symbols: real part; open symbols: imaginary part.)

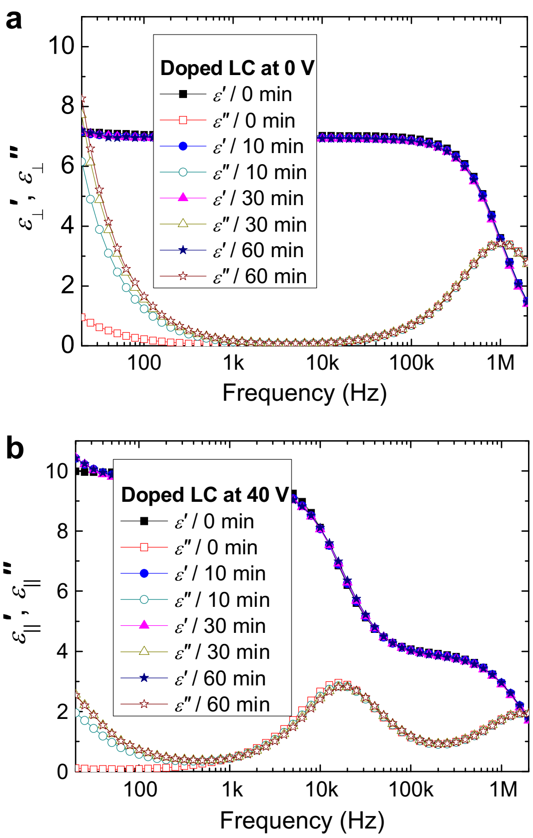

Fig. 5. Dielectric spectra of the LC–dye composite at a biased voltage of (a) 0 V and (b) 40 V for various times of illumination.

Table 1
Fitting parameters of the HN model for cells under illumination of various accumulated durations and voltage bias of 40 V.

Sample	Feature	Time (min)	β	γ	f_c (Hz)	Dielectric strength
LC		All ranges	0.98	1	16 507	6.01
LC + MR						
	First relaxation	10	1	0.79	0.91	24.35
		20	1	0.83	3.29	11.69
		30	1	0.85	4.67	10.00
		40	1	0.85	4.66	10.11
		50	1	0.84	4.68	9.75
		60	1	0.84	4.76	9.70
	Second relaxation	10	0.99	1	16 939	5.67
		20	0.99	1	17 029	5.63
		30	0.99	1	17 495	5.61
		40	0.99	1	17 434	5.60
		50	0.99	1	17 346	5.61
		60	0.99	1	18 023	5.61

The dielectric complex spectrum can be formulated by the Havriliak–Negami (HN) model in the following equation [19]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left(1+(i\omega\tau)^\beta\right)^\gamma} \tag{2}$$

where ε_∞ is the high-frequency permittivity, $\Delta\varepsilon$ is termed the dielectric strength defined as the difference between the static (or low-frequency) permittivity ε_s and ε_∞, ω ($= 2\pi f$) is the angular frequency, τ ($= 1/2(\pi)f_c$) is the relaxation time, and the exponents β and γ are the symmetry and asymmetry parameters of the equation describing the distribution of the relaxation times, respectively. This model satisfies the linear superposition, so it can describe many relaxation behaviors in one material. The measured results of the dielectric spectra can be fitted nicely by the HN model (i.e., Eq. (2)), and the material nature can, thus, be discussed from the fitting parameters. As such, the HN model can be utilized to acquire useful information on the dielectric properties, such as the dielectric strength, the relaxation time, and the symmetry and asymmetry parameters. Table 1 shows the results of the curve fitting with coefficients of determination $r^2 > 0.98$. An exemplary HN plot is shown in Fig. 7 to demonstrate the validity of the model. The constant crossover frequency of the neat DFLC indicates that the cell temperature does not change appreciably or the cell does not absorb the heat effectively (see Table 1). For the dye-doped DFLC cell, both the first relaxation frequency and the dielectric strength become stable within 30 min when the accumulated illumination time increases. (The relaxation frequency for saturated MR isomerization is at about 4.7 Hz, and the corresponding dielectric strength is about 10). On the other hand, the second relaxation time and dielectric strength do not vary significantly with the illumination time as displayed in the table. It is likely that some changes in molecular packing due to the MR transformation will have an effect on the frequency of the second relaxation mode. After all, despite poorer packing into the host LC molecules, the *cis* state may enlarge the molecular distance, permitting the ease of rotation about the short molecular axis until the structure becomes stable again, after a prolonged irradiation. Table 1 cannot provide clear evidence of the

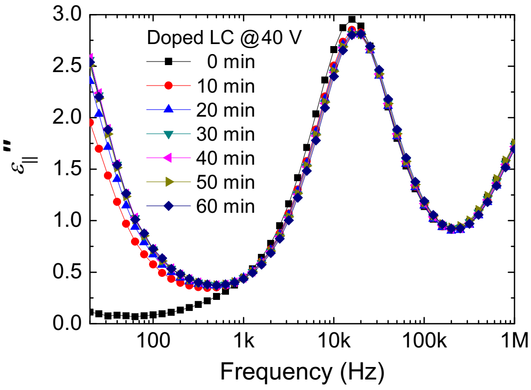

Fig. 6. Dielectric losses of the LC–dye composite for various illumination times at bias 40 V.

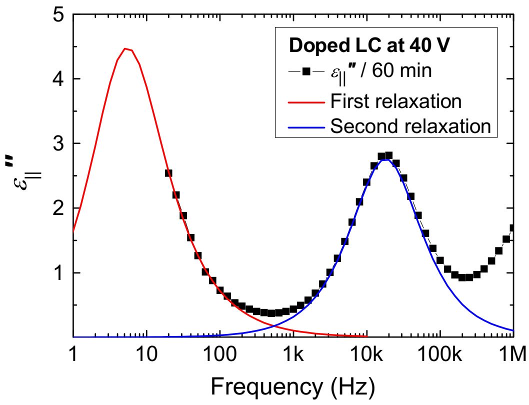

Fig. 7. Typical plot showing the fitted result for the 60-min-irradiation experimental data by the HN model.

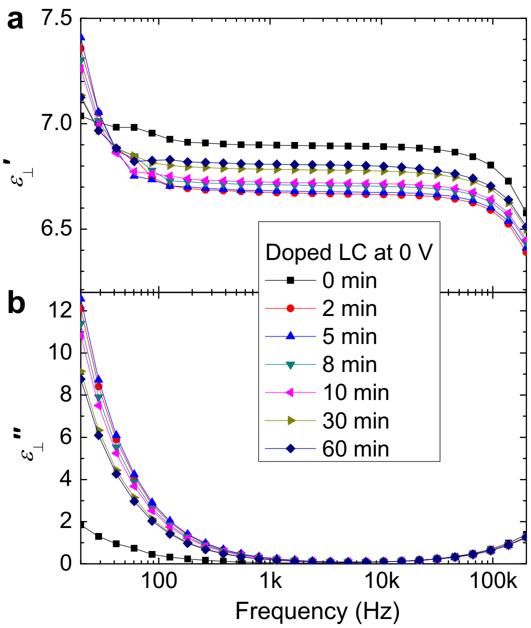

Fig. 8. Dynamic measurement of the dielectric (a) real part and (b) imaginary part under bias 0 V.

successive rise and fall of the relaxation frequency for such a mechanism, though.

The experimental results discussed above were acquired by accumulating the exposure time with brief interruptions for dielectric measurements. It would be interesting to compare these results with those obtained in real time in the dynamic process of the *trans*-to-*cis* isomerization, i.e., where the illumination process continues when a dielectric measurement is taken. For this purpose, we managed to shorten the measurement time down to about 25 s for each dielectric spectrum in expense of the data points. Figs. 8 and 9 show the dynamic measurements of the dielectric spectra of the doped DFLC at 0 and 40 V, respectively. Note that the continuous illumination leads to a more dramatic alteration in the whole spectral range. Fig. 9(b) shows the imaginary part of the dielectric spectrum; it reveals that the crossover frequency changes appreciably with the time of continuous laser illumination. Fig. 10 displays the strong continuous-illumination-time dependence of the fitted crossover frequency using the HN model and the corresponding temperature deduced in accordance with the Arrhenius equation. The figure shows a sharp increase in crossover frequency within a couple of minutes followed by a concave-up monotonic decay, as can be visualized in the temperature plot based on Eq. (1). This result implies that the MR structural transformation soon takes place to increasingly induce local heating of the LC molecules right after the onset of laser irradiation. The gradually reduced population of the *trans* molecules then slows down the buildup of heat. The temperature tends to drop to a seeming constant eventually, reflecting the equilibrium temperature in association with the laser power.

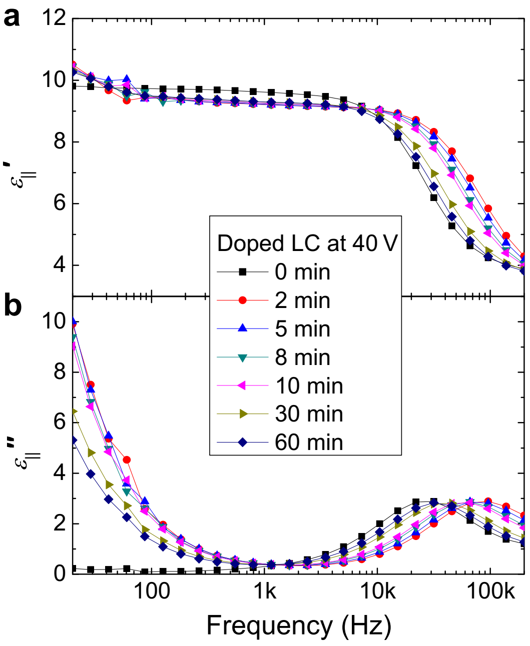

Fig. 9. Dynamic measurement of the dielectric (a) real part and (b) imaginary part under bias 40 V.

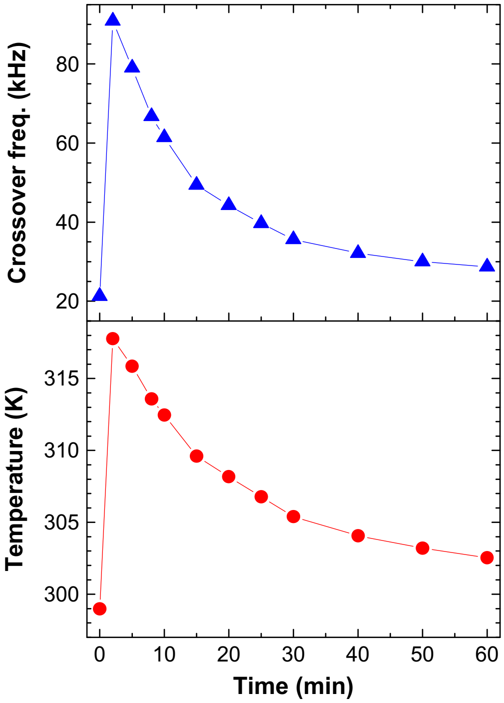

Fig. 10. Fitted results of the crossover frequency (top) and the corresponding temperature (bottom) of the dye-doped DFLC versus the dynamic laser irradiation time.

4. Conclusions

In conclusion, the dielectric properties of a DFLC cell doped with C.I. Acid Red 2 (at 0.5 wt%) have been investigated. The dielectric spectrum of the LC–dye composite system can be divided into three sections, manifesting the ion-diffusion, LC-material and the ITO effects. Under illumination by an argon-ion laser operating at irradiance of 550 mW cm^{-2} and wavelength of 514.5 nm, the dielectric spectrum of the undoped counterpart is virtually unaffected, whereas the dielectric spectrum of the azo-dye-doped DFLC shows a pronounced feature corresponding to the dielectric relaxation of isomerization of the dye molecules in the low-frequency region. The relaxation frequency of the photoisomeric process under bias 40 V is deduced to be about 5 Hz through data fitting with the HN model. With the illumination time increasing beyond ~30 min, the low-frequency peak of the dielectric imaginary spectrum reaches the saturation because the majority of MR molecules accomplish the isomerization. Moreover, by using the properties of a DFLC, the dynamic process of the dye isomerization can be observed in a real-time fashion. The experimental result shows that the temperature of the cell increases steeply at first and then decreases with increasing time of continuous laser irradiation. It implies that the cell absorbs energy very quickly at the beginning of laser irradiation. The extent of MR isomerization can be monitored by low-frequency dielectric spectroscopy of dye-doped LCs.

Acknowledgements

This on-going research is partially supported by the National Science Council of Taiwan, the Republic of China under Grant No. NSC 98-2112-M-033-004-MY3.

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