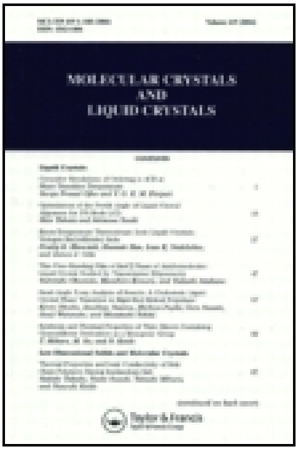

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Temperature-Dependent Electric Characteristics in an E7/CNT Colloid

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Temperature-Dependent Electric Characteristics in an E7/CNT Colloid

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Temperature effects on the electric characteristics were studied in a colloidal system made up of 0.05-wt.% multiwalled carbon nanotubes dispersed in the nematic liquid crystal E7. The electric properties were observed via measurement of transient current in a homogeneously aligned liquid-crystal cell induced by a polarity-reversed field. The cell filled with the suspension and that containing pristine liquid crystal exhibited similar voltage- and temperature-dependent behaviors in the experiments. However, it was interestingly found that the transient current originating from the transport of impurity ions was remarkably suppressed in the suspension. The enhancement of the ionic mobility was also observed in such a colloidal system.

Keywords: carbon nanotubes; colloid; electronic transport; transient current

Not for a long time, displays based on liquid crystal have now established a firm foothold on the market as flat panel displays for computers, transportation, communications, instrumentation and, getting more and more popular in recent years, for televisions since the first liquid-crystal display device and commercial liquid-crystal display watches appeared in 1968 and 1970, respectively. Even though liquid-crystal displays have become a part of our daily life, there are still many problems to deal with and much space to improve in the relevant research area. Due to the need of high-quality image performance, the nematic liquid crystal used in a high-information-content

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display device is required to possess high resistivity such that an applied voltage can be held without a leakage current, thus preventing the flickering of images. Moreover, the liquid crystal employed in an active-matrix device should have low impurity-ion concentration because the impurity ions, often adsorbed on the alignment layers in a nematic liquid-crystal cell even if they are not in the influence of an externally applied electric field, can generate a nontrivial net (residual) dc voltage, causing image-sticking problems. Indeed, the impurity ions in the liquid-crystal cell are a nuisance, which can tremendously worsen a display's performance, leading to the degradation of the image quality [1–3]. Unfortunately, the excess ions in a display cell may come from various sources and their existence can not simply be avoided technically. As such, the electric transport of the impurity ions and the resulting electric properties of a nematic liquid crystal should be considered as important issues in the research and development of liquid crystals for photonic applications. It has been found in some earlier woks, via the method of transient-current measurement, that the spatial distribution of ionic carrier mobility is dependent on the director orientation [4–6] as well as the electric double-layer thickness [7]. It has been suggested that the behavior of transient current in the liquid-crystal cell is governed by the carrier mobility.

There are a number of ways to reduce the unwanted ion effects, including the development of new liquid-crystalline materials, purification of liquid crystals, rigorous cell manufacturing process, appropriate design of driving circuits, and the doping of ion-trapping additives such as nanoparticles dispersed in a liquid crystal cell [8–12]. Our earlier efforts at investigations of guest-host colloidal systems of carbon nanotubes suspended in a nematic liquid-crystal hydrosol revealed that carbon nanotubes as a dopant can provide high photosensitivity and larger nonlinear optical responses and, in turn, enhance the orientational photorefractivity of the liquid crystal [13–15]. Along this line of research aiming at these alluring suspension systems, we have accidentally discovered that a minute addition of multiwalled carbon nanotubes in a liquid-crystal display cell is capable of suppressing the undesired ion effects presumably due to sufficient ion trapping via charge transfer [8–12]. The effects of carbon nanotubes as a dopant on the electro-optical and electrical properties of the cell are particularly manifested by means of cyano-based liquid crystals driven by dc voltage [8]. The observations of the decrease of driving voltage, suppression of backflow effect as well as repression of field screening in said nanotube-doped colloidal systems imply that the charge density of the liquid-crystal host are modified by incorporation with nanoscale materials. Such rectification will alter the behavior of transient current induced by a sudden change in applied voltage in that the electric double-layer thickness strongly depends on it [16].

In this article, we report on observations of transient currents in carbon-nanotube doped nematic liquid crystals under certain experimental conditions for the polarity-reversal of an externally applied electric field. We show the experimental results on voltage- and temperature-dependent transient currents and discuss the transient behavior of current peaks in nematic liquid-crystal cells. The charge mobility is then deduced via a simple formula with some simplified assumptions from the transient-current data. By comparison of the results between the doped and neat cells, it is found that carbon nanotubes have the ability to assist nematic molecules to orient and enhance the drift mobility of the charged ions in the cell.

The empty cell was manufactured with two flat glass substrates whose inner surfaces were covered with indium–tin oxide (ITO) and then spincoated with polyimide for planar alignment. Pairs of rubbed substrates were assembled in an antiparallel configuration where a cell gap d of $5.6\,\mu$m was ensured by ball spacers. A small quantity ($\sim$0.05 wt.%) of treated, highly purified multiwalled carbon nanotubes was added to the eutectic nematic E7 with dielectric anisotropy $\Delta\varepsilon = 13.1$ at 1 kHz. Details of the carbon-nanotube material and the treatment are given elsewhere [10]. The mixture was introduced into empty cells by capillary action in the isotropic phase and then allowed to cool down at room temperature. The bulk resistance of the cell was deduced to be about 400 MΩ in accordance with the resistivity of $2.4 \times 10^{11}\ \Omega \cdot \text{cm}$ as provided by Merck's datasheet. As a reference, cells composed of pristine E7 were also prepared.

Transient currents in undoped and doped cells were measured through a 2-MΩ load resistor in series by means of a digital oscilloscope at various temperatures. Note that the load resistance is quite small compared with the liquid-crystal bulk resistance and yet it is large enough to yield a significant signal-to-noise ratio for the voltage signals. The external polarity-reversed voltage, resembling a signum function between -5 s and $+5$ s, was applied across the cell thickness by an arbitrary waveform function generator. The cell temperature T was controlled in an oven connected to a thermoregulator to ensure the thermal stability and uniformity of the whole cell.

Typical transient-current curves induced by a polarity-reversed voltage V greater than the Fréedericksz threshold V_{th} at various temperatures are shown in Figure 1. At first, upon the onset of the polarity reversal, normal charging current appears within about

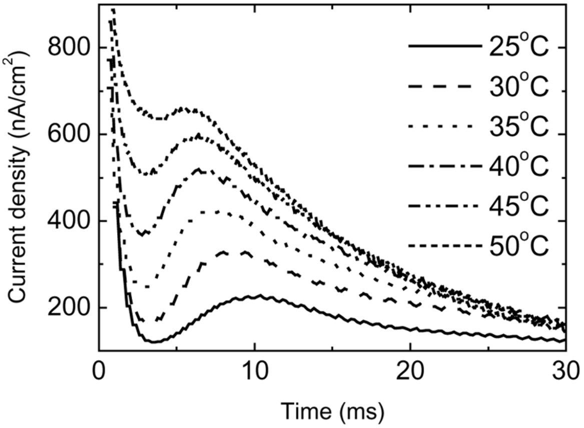


FIGURE 1 Transient currents in a neat E7 cell under the influence of an applied, polarity-reversed voltage of 2 V at various temperatures.

several milliseconds and then a current peak is observed. For a dielectric capacitor in a circuit, the charging current decays as a single exponential function of time. Although it could be more complicated for the case of the liquid crystal sandwiched between ITO-coated glass plates (regarded as a parallel-plate capacitor), the normal charging current which is limited by the response time of the sample as well as the measuring circuit can, nevertheless, be approximated by a *single* exponential. It is worth pointing out that two components form the transient current—the conduction current as the baseline and the director-orientation-disturbed displacement current as the peak current. The conduction current is also subject to the resistance of the sample and the measuring circuit as the normal charging current is. It refers to the passage of *free* electric charges through the cell under the influence of an electric field and is caused by drift motion of conduction electrons. The displacement current, arising from the time rate of change in electric displacement in the liquid-crystal bulk, is mainly attributed to the bound charges; i.e., the impurity ions. Once the polarity of the electric field reverses, the orientations of the anisotropic liquid-crystal molecules are disturbed as the electric flux density in the cell suddenly changes. The current peak is thus induced. The two components of the current mentioned above can be summed up in the following equation [17]:

$$J(t) = \frac{\mathrm{d}}{\mathrm{d}t}\left[\int_{-d/2}^{1/2} \varepsilon_0 \varepsilon_{\mathrm{eff}}(\theta) E(z,t)\,\mathrm{d}z\right] + \rho \exp(-t/t_{\mathrm{p}})\mu \int_{-d/2}^{1/2} E(z,t)\,\mathrm{d}z, \quad (1)$$

where $J(t)$ is in $\mathrm{Cm}^{-1}\mathrm{s}^{-1}$ in the SI unit, $\varepsilon_{\mathrm{eff}}$ is the effective dielectric constant expressed as $\varepsilon_{\mathrm{eff}} = \varepsilon \sin^2\theta(z,\ t) + \varepsilon \cos^2\theta(z,\ t)$ (θ is the angle between the substrate and the director), $E(z,\ t) = D(z,\ t)/\varepsilon_0\varepsilon_{\mathrm{eff}}$, ρ is the volume density of free charge to cover a distance of d, and the drift-current mobility $\mu = d^2/t_{\mathrm{p}}V$, where the peak time t_{P} stands for the time needed for an ion to drift from one glass substrate to the other. Obviously, the first term at the right-hand side of Eq. (1) represents the displacement current and the second term stands for the conduction current. It can be seen from Figure 1 that the intensity of the conduction current, represented by the baseline of each curve, is affected by temperature. As the ambient temperature is elevated, the viscosity of the liquid crystal is reduced while the ability of diffusion and drift of the charges is increased, leading to a more intense conduction current. On the other hand, the displacement current, giving the peak in each curve and appearing in a few tens of milliseconds or less, occurs earlier as the temperature rises. We define the time the maximal current occur in the peak as the peak time. Figure 1 illustrates that the peak time becomes shorter as the temperature becomes higher.

Figure 2 compares the transient currents observed in an E7 cell and a nanotube-doped counterpart at a constant temperature of 25°C. It can be found that the peak current density attributed to space-limited charges is reduced in the cell doped with multiwalled carbon nanotubes while it is submitted to a polarity-reversed field. (The transient-current curve attributed to the space-limited charge alone can be

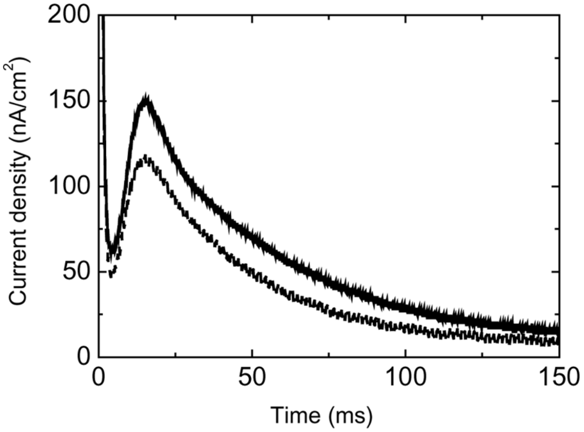
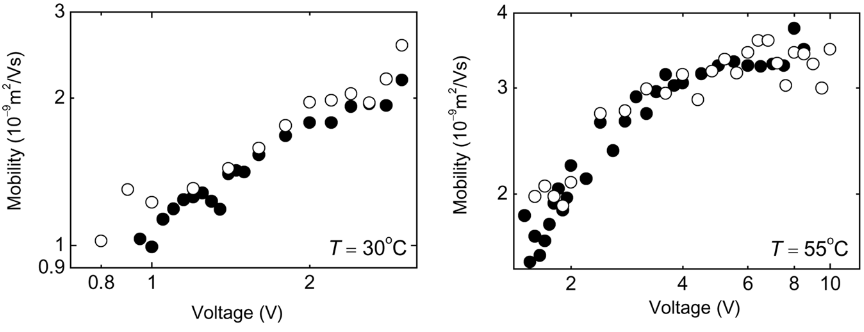


FIGURE 2 Transient currents in neat E7 (solid line) and CNT-doped (dashed line) cells at 25°C submitted to a polarity-reversed voltage of 1.5 V.

obtained after subtracting the baseline attributable to the normal charging current and conduction current from the measured current signals.) This implies that the motion of the impurity ions which are responsible for the peak current is restricted by the carbon-nanotube dopant. With strong electron affinity of carbon nanotubes dispersed in the liquid crystal constituted of polar alkylcyano molecules, many charge-transfer complexes can easily be formed through intermolecular interaction in the colloidal system, as evidenced by ultraviolet absorption and ultraviolet/visible fluorescence spectroscopy [18]. Density functional calculations within local density approximation have also suggested that the strong anchoring via inter-molecular hydrogen bonding induces a self-alignment of carbon nanotubes in the LC [19]. It is pity that, in this analytical study, only one specific case, a (5, 5) armchair singlewalled nanotube, was considered and the other important types of nanotubes; i.e., zigzag and the most commonly encountered chiral types as well as multiwalled analogues, were left untouched [19]. The multiwalled carbon nanotubes serving as ion-trapping agent generate a significant trapping-site density, permitting the observed amount of moving charges to decrease as a result of rectification of interface properties. In other words, the nanotube dopant suppresses the double-layer effect. It can be thought that, with the presence of the "jailers" (namely, carbon nanotubes as the ion trappers) in the colloidal system, a substantial portion of the ion charge is "arrested" or in "captivity" in the liquid-crystal "cell." This result is consistent with our recently published work [12].

In order to take advantages from the transient-current data, the mean free path of the ions in the cell being nearly equal to the cell gap d is assumed. This allows one to determine the mobility of the impurity ions, defined as the magnitude of the drift velocity per unit electric field. The ionic mobility μ for an external voltage V can be calculated via the simplified equation $\mu = d^2/t_P V$. As one can see from Figure 3, the ionic mobilities increase with increasing applied voltage in that the impurity ions experience higher mobility along the direction of the liquid-crystal molecular axes in a stronger field [12,20], where the nematic directors become more parallel to the field. Although the data points seem to scatter slightly, Figure 3(a) doubtlessly shows that the mobility in a doped cell is higher than that in a neat one. This implies that the orientation of the nematic molecules in the suspension is more parallel to the applied electric field. It is likely that carbon nanotubes can help the liquid-crystal molecules to tilt under the influence of the field because the elongated carbon nanotubes tend to orient in parallel to the field. Experimental observations have shown that either singlewalled or multiwalled carbon nanotubes



(a) (b)

FIGURE 3 Ionic mobilities depending on the applied voltage in a neat E7 cell (●) and a nanotube-doped cell (○) at (a) 30°C and (b) 55°C.

dispersed in nematic liquid-crystal solvents are orientationally ordered by the nematic matrix and are preferably parallel to the liquid-crystal director in null external field [18,21]. At least, the presence of the nanotube dopant yields a relatively higher effective voltage for the liquid-crystal bulk [8,12].

While the temperature approaches the clearing point, the viscosity becomes smaller and conduction current becomes greater. Under the condition of high temperature, the trapped impurity ions possess enough energy to escape from the trapping sites. (The originally immobile charges are librated by thermal energy to become mobile.) So the advantage of the nanotube dopant, used to facilitate the orientation of

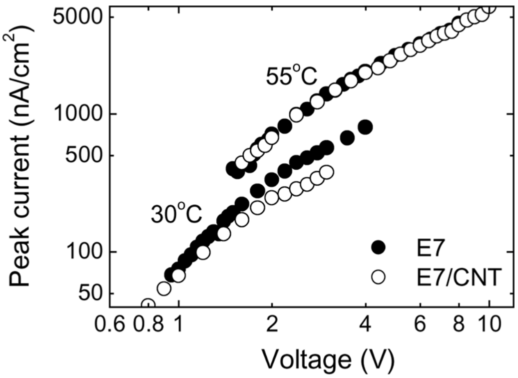


FIGURE 4 Voltage-dependent peak currents in a neat E7 cell (●) and a nanotube-doped cell (○) at 30°C and 55°C.

liquid-crystal molecules, becomes less pronounced or even negligible as the ambient temperature is increased to a value near the clearing point (see Fig. 3(b)). This means that at 55°C approaching to the clearing point of E7 the two transient-current curves coincide, yielding the peak-current plots as shown in Figure 4.

In conclusion, the electric behavior of a pristine liquid crystal and a carbon-nanotube colloidal system were studied by the method of transient-current measurement. Both temperature- and voltage-dependent features are presented in this work. Experimental evidence shows that adding multiwalled carbon nanotubes as a dopant can serve as an impurity-ion trapping agent in a liquid-crystal display cell and, in turn, suppress the field-screening effect. In addition, the parallel-to-field orientation of carbon nanotubes may aid the orientation of liquid-crystal molecules under the influence of an applied electric field and give the essential gain of the ionic mobility. Furthermore, the trapping efficiency is seriously challenged at higher temperatures.

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