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Temperature dependence of electro-optical characteristics of polymer dispersed liquid crystal films

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Polymer dispersed liquid crystal (PDLC) films consist of microdroplets of a liquid crystal dispersed in a polymer matrix. Their applications are based on the electrically controllable light scattering properties of the liquid crystal droplets. The effects of temperature on the electro-optical properties of PDLC films have been rarely investigated. In this work, we studied the light transmission on varying the temperature and frequency. It was observed that the transmission at a fixed voltage decreased with increasing temperature above 43°C, independent of frequency. We examined possible origins of this unusual dependence of the transmission on the temperature. It was concluded that conductivity effects due to free ions newly created at high temperatures could be responsible for the unusual behaviour observed.

1. Introduction

Since the early 1980s, polymer dispersed liquid crystals (PDLCs) have become the subject of scientific investigation amongst physicists, chemists, and material scientists [1–6]. PDLCs, consisting of micron-sized liquid crystal droplets embedded in a polymer matrix, have many characteristics suitable for reflective displays, light windows, and holographic gratings [5, 7–10]. Basically their applications are based on the electrically controllable light scattering properties of liquid crystal droplets, which differ from traditional liquid crystal devices in many ways. The light scattering properties of PDLC films depend strongly on many parameters associated with film fabrication. These preparation parameters include droplet size, shape and number density, the LC and polymer refractive indices, etc. [11–15]. Interfacial effects are also important due to the increased surface-to-volume ratio of PDLCs.

A variety of ways have been developed to produce PDLC films. One of the most widely employed schemes in their fabrication is the polymerization-induced phase separation method (PIPS), which was pioneered by Doane and other workers [5, 16, 17]. In this scheme, a homogeneous mixture of a liquid crystal and a prepolymer containing an appropriate amount of initiator is initially prepared. Then, polymerization is induced through the application of heat or UV irradiation, depending on the type of initiator. As the polymerization proceeds, the liquid crystal separates from the polymer matrix to form droplets or other shapes, depending on the preparation conditions. Variations in the phase separation process can lead to different morphologies, which have profound effects on the electro-optical characteristics of the PDLC films.

Though intensive investigations have been made, many areas are still poorly understood and remain to be more fully studied to allow for the development of reliable and stable PDLC devices. In particular, the effects of temperature on the electro-optical properties has been investigated rarely. Amundson has studied the transmission at various temperatures for PDLC films based on E7/NOA65 [12]. The PDLC films had a typical morphology with droplet sizes around 1–5 μm in diameter. No unusual behaviour was observed, and the switching voltage decreased monotonously with increasing temperature. Fuh *et al.* investigated PDLC films based on E7/EPO305 and found that a plot of transmission as a function of temperature showed broad peaks [18]. The authors attributed this unusual dependence of transmission on temperature to the variations in the refractive indices of the polymer matrix and the LC droplets.

These previous studies demonstrate that subtle differences, despite similar LC components and film morphologies, can lead to substantially different temperature dependences of the electro-optical properties. Recently, PDLC systems made from TL mixture and PN393 have received intensive attention. This PDLC system allows a high loading of TL mixtures and shows a strong dependence of droplet size on composition. More interestingly, this PDLC system has a thin-walled, foam-like morphology due to the high concentration of the liquid crystal. Motivated by several surprising features of this novel

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PDLC system, we fabricated PDLC films consisting of TL213/PN393. The primary objective of this work is to investigate the temperature dependence of their electro-optical properties and explain the experimental results.

2. Experimental

PDLC films can be fabricated in a variety of ways. In this work, the PIPS method was used to prepare PDLC films from a commercially available liquid crystal mixture (TL213) and a UV-curable prepolymer material (PN393). TL213 contains superfluorinated biphenyl and terphenyls, and PN393 is a mixture of mono- and multi-functional acrylates. The nematic–isotropic transition temperature, $T_{\text{N-I}}$, for TL213 is 87°C. First, homogeneous mixtures of TL213 and PN393 were introduced into a thin gap between two indium tin oxide (ITO) coated glass plates by capillary action. The cell gap was controlled by using 13 μm glass microsphere spacers. The films were then cured by UV irradiation using a mercury arc lamp. UV light in the wavelength range 340–360 nm was selected using appropriate filters. The UV intensity was 5–10 mW cm^{-2}, and the polymerization temperature was 26–30°C. The fabricated films have a thin-walled, foam-like morphology with droplet sizes 1–5 μm in diameter.

The electro-optical properties of the PDLC films were measured using a He-Ne laser and a photodetector. The sample temperature was controlled within ±0.5 K with a Janis Cryostat (Model VPF-475) equipped with a temperature controller (Model 330, Lake Shore). The PDLC morphology was studied using an optical microscope equipped with a camera (Model CH40, Olympus).

3. Results and discussion

In the present work, the voltage dependence of the light transmission has been studied at various temperatures for a film of concentration 82.9 wt % TL213, see figures 1 and 2. A He-Ne laser at 632.8 nm was used as a light source. As the temperature was increased to 43°C, the transmission curves shifted to lower voltages. However, it is interesting to note that as the temperature was increased further, the transmission curves shifted back to higher voltages. As described previously, a similar dependence of the transmission on temperature was observed for a PDLC film consisting of E7/EPO305 [18]. The authors explained the strange behaviour in terms of the dependence of the refractive index mismatching between the polymer matrix and the liquid crystal droplets on temperature. In this work, we focus on this unusual observation and seek a fuller explanation.

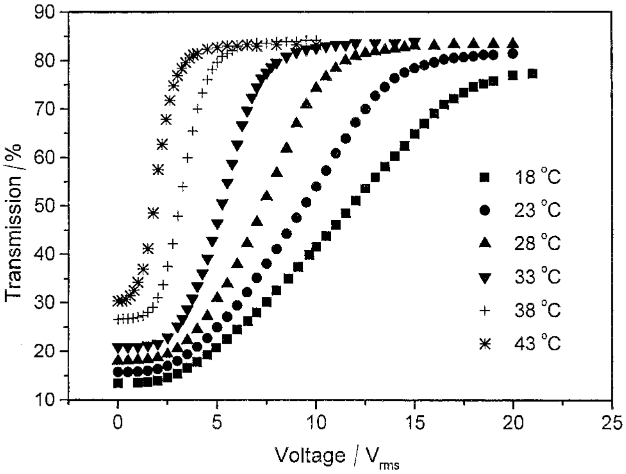

Figure 1. Transmission versus the applied voltage (1 kHz) at various temperatures (18–43°C) for the film containing 82.9 wt % TL213.

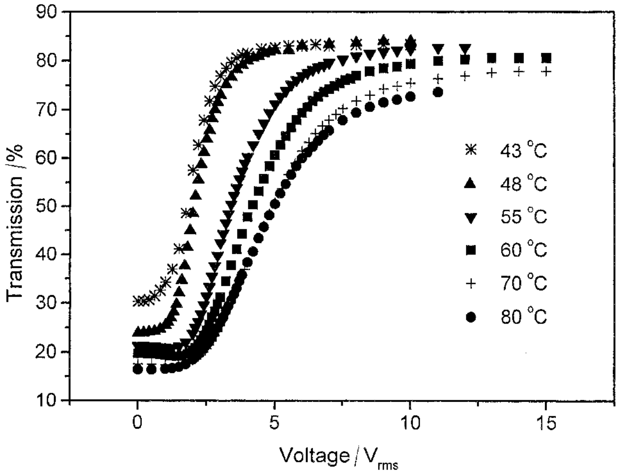

Figure 2. Transmission versus the applied voltage (1 kHz) at various temperatures (43–80°C) for the film containing 82.9 wt % TL213.

As a first step, it is reasonable to account for the unusual behaviour on the basis of the change in the switching voltage of the PDLC film. A physical model to quantify the switching voltage has been developed for slightly elongated droplets by equating the electric field energy and the elastic energy. According to this physical model, an expression for the switching voltage in the strong anchoring limit is given by [12, 19, 20]:

$$V_{\text{switch}} = \frac{1}{c}\frac{d}{R}(L^2-1)^{1/2}\left(\frac{K}{\varepsilon_0 \Delta\varepsilon}\right)^{1/2}, \qquad (1)$$

where R is the droplet radius, d the film thickness, L the droplet anisotropy (ratio of the major to minor radius) in the case of an ellipsoid, $\Delta\varepsilon$ the dielectric anisotropy of the liquid crystal, ε_0 the free-space permittivity, and K the effective elastic constant. The prefactor $1/c$ is related to the effectiveness of the field across the droplets due to a dielectric or conductivity mismatch between the LC droplets and the surrounding polymer matrix. The prefactor c is given by $3\varepsilon_p/(\varepsilon_{LC}+2\varepsilon_p)$, the value of which is of the order of unity in the dielectric region. The subscripts p and LC refer to the polymer matrix and the liquid crystal component, respectively.

In the temperature range 18 to 43°C, the observed decrease in V_{switch} with increasing temperature can be explained qualitatively in terms of equation (1). If only the temperature dependent terms in equation (1) are considered, then V_{switch} is proportional to $(K/\Delta\varepsilon)^{1/2}$ with $K \sim S^2$ and $\Delta\varepsilon \sim S$ [21, 22]. Because the order parameter S of liquid crystals decreases strongly with increasing temperature, the switching voltage is expected to decrease, as observed in figure 1. However, it should be noted that the variations in V_{switch} at temperatures above 43°C are apparently inconsistent with equation (1).

For a closer examination of the temperature dependence, the variations in V_{th}, V_{10}, V_{50} and V_{90} with respect to the temperature were plotted, see figure 3, where V_{th} refers to the threshold voltage. V_{10}, V_{50} and V_{90} refer to the applied voltages required to achieve 10%, 50% and 90% of the ultimate transmission at saturating voltages, respectively. All the characteristic voltages reached minimum values at 43°C, and the rate of decrease was in the order V_{90}, V_{50}, V_{10} and V_{th} in the low temperature region (18–43°C). In addition, a plot of transmission versus temperature for various voltages, is given in figure 4. Corresponding peaks can be observed near 43°C. The peaks were most pronounced in the low voltage region (2–4 V) and gradually became broader and smaller as the applied voltage was increased. It is apparent from figures 3 and 4 that some changes, which effect the optical properties of the PDLC film, take place at temperatures higher than 43°C. Similar results were obtained for a PDLC film having 80 wt % TL213 and a 10 μm cell gap, see figure 5.

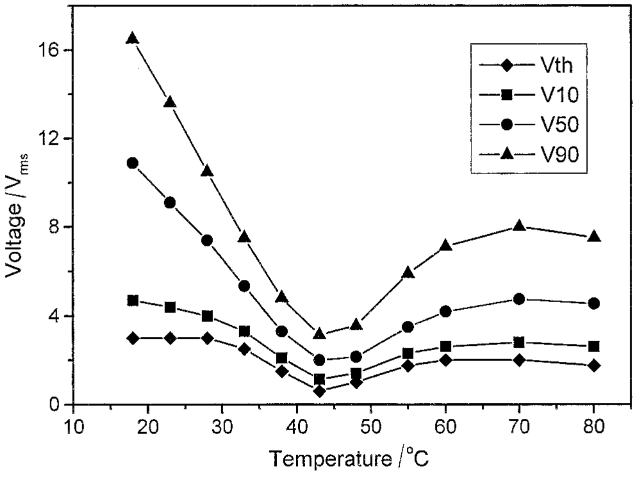

Figure 3. Variations in V_{th}, V_{10}, V_{50} and V_{90} with temperature for the film containing 82.9 wt % TL213.

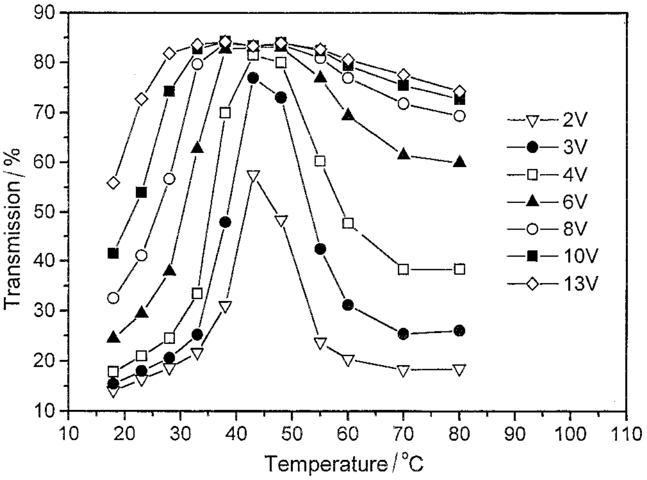

Figure 4. A plot of transmission versus temperature for the film containing 82.9 wt % TL213 for various voltages.

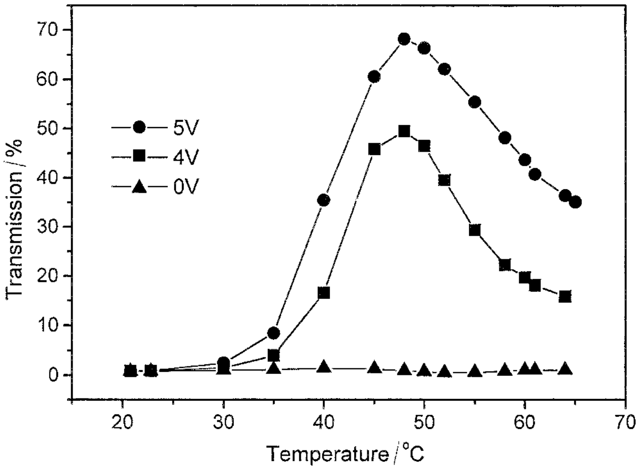

Figure 5. A plot of transmission versus temperature for the film with 80 wt % TL213 for various voltages.

One conceivable reason for this unusual behaviour may be the temperature dependence of the refractive indices of the polymer matrix and the LC droplets. In principle, the on-state transmission of PDLC films depends strongly on the difference between the effective refractive index of the droplet, n_{eff}, and the refractive index of the polymer matrix, n_p. Because n_{eff} approaches the ordinary refractive index of the liquid crystal, n_o, at saturating voltages, a high degree of transparency in PDLC films is achieved only when n_p is equal to n_o. Therefore, if the degree of refractive index mismatching between the polymer matrix and the LC droplets depends considerably on temperature, the transmission is also expected to show a corresponding temperature dependence. Figure 6 shows the dependence of the refractive indices of the nematic liquid crystal TL213 and the polymer PN393 on temperature. The effective refractive index of a LC droplet, n_{eff}, which the incident

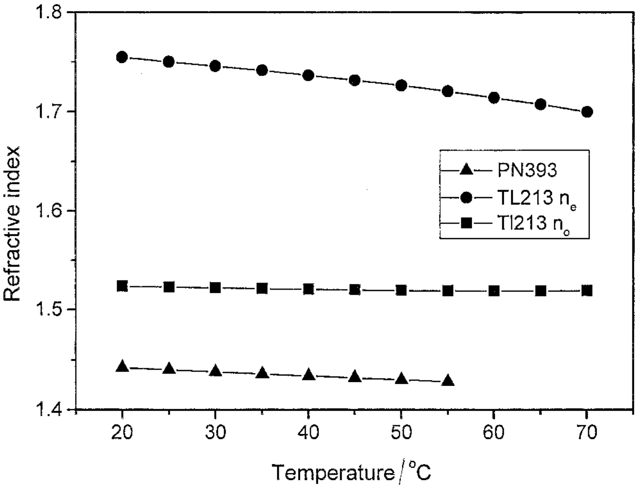

Figure 6. Dependences of the refractive indices of the nematic liquid crystal TL213 and the prepolymer PN393 on temperature.

light 'sees' is given by [6]

$$n_{\mathrm{eff}}=\frac{n_{\mathrm{o}}n_{\mathrm{e}}}{(n_{\mathrm{o}}^2\sin^2\theta+n_{\mathrm{e}}^2\cos^2\theta)^{1/2}} \tag{2}$$

where θ is the angle between the incident light and the director axis of a LC droplet. Here, n_{o} and n_{e} are the refractive indices of the nematic LC when the incident light is parallel and perpendicular to the director vector, respectively. If we take into account that some amount of TL213 is usually dissolved in the polymer matrix, the actual refractive index of PN393 should be slightly larger than the nominal value. For example, when the concentration of the dissolved TL213 is 20 wt %, n_{p} can be increased to about 1.5. However, since $n_{\mathrm{p}}\leqslant n_{\mathrm{o}}\leqslant n_{\mathrm{eff}}\leqslant n_{\mathrm{e}}$ even in this case, it is evident from figure 6 that the temperature dependence of the refractive index mismatching is negligible and therefore is not the origin of the unusual behaviour seen for the transmission.

Another possible explanation may involve light scattering by director fluctuations. It is well known that fluctuations in the orientation of the director, **n**, in a nematic LC give rise to strong light scattering. In the limiting case that the dielectric anisotropy, $\delta\varepsilon=\varepsilon_{\mathrm{e}}-\varepsilon_{\mathrm{o}}$, is small, the scattering cross-section for a bulk nematic LC is given by [23]

$$\sigma\sim A\frac{k_{\mathrm{B}}T}{q^2}\left(\frac{\delta\varepsilon^2(q)}{K}\right) \tag{3}$$

where A is a constant, K the elastic constant, q the scattering vector, and k_{B} the Boltzmann constant. Here, $\delta\varepsilon(q)$ is defined as the dielectric anisotropy in q-space. Because $K\sim S^2$ and $\delta\varepsilon(q)\sim S$ (at fixed q) where S is the order parameter [21, 22], σ is only weakly dependent on temperature. It is reasonable to assume that the temperature dependence of σ for a PDLC system does not deviate significantly from equation (3). Hence, the director fluctuation is not likely to cause the strong dependence of the transmission on temperature.

An alternative explanation considers the variation of the effective field across the LC droplets. There are many effects which influence the effective field across the droplets. For example, movements of mobile ions and other depolarization effects within the PDLC film, can change the effective field across the droplets. The electro-optical properties of PDLC films are determined by their dielectric and resistive responses to the applied field. Typical dielectric effects, which are non-dissipative and out of phase with the applied field, are related to the reorientation of LC molecules and the depolarization charges within the polymer and the liquid crystal. In comparison, resistive effects, which are dissipative and in phase with the applied field, include the movements of ions through the polymer and the liquid crystal and viscous drag during the reorientation.

As a first step in checking this suggestion, we observed the PDLC film using an optical microscope with crossed polarizers while varying the temperature at a fixed applied voltage of 4 $\mathrm{V_{rms}}$. It was seen clearly that the transmitted light through each droplet became gradually brighter on increasing temperature above 43°C. This observation shows that the degree of alignment of the LC molecules within the LC droplets was reduced. This reduction is believed to result from the decrease in the effective voltage across the droplets.

The effective fields across LC droplets have been studied previously [20, 24]. Given the assumption that the dielectric constant (or conductivity) of the nematic LC may be approximated as that of an isotropic LC, the effective field across a nematic droplet can be expressed as

$$E_{\mathrm{eff}}=E_{\mathrm{a}}\frac{3\varepsilon_{\mathrm{p}}}{2\varepsilon_{\mathrm{p}}+\varepsilon_{\mathrm{LC}}}(\omega\rightarrow\infty) \tag{4a}$$

$$=E_{\mathrm{a}}\frac{3\sigma_{\mathrm{p}}}{2\sigma_{\mathrm{p}}+\sigma_{\mathrm{LC}}}(\omega\rightarrow 0) \tag{4b}$$

where E_{eff} and E_{a} refer to the actual electric field across the droplets and the applied electric field, respectively. ε_{p} and $\varepsilon_{\mathrm{LC}}$ are the dielectric constants, and σ_{p} and σ_{LC} the conductivities of the polymer matrix and the liquid crystal, respectively.

In order to identify the precise cause for the reduced voltage across the droplets, we measured the transmission for the cell with 82.9 wt % TL213 concentration as a function of frequency at various temperatures, see figure 7. When an external field is applied across the film, mobile ions with different polarities are accelerated in opposite directions. This in turn sets up a depolarization

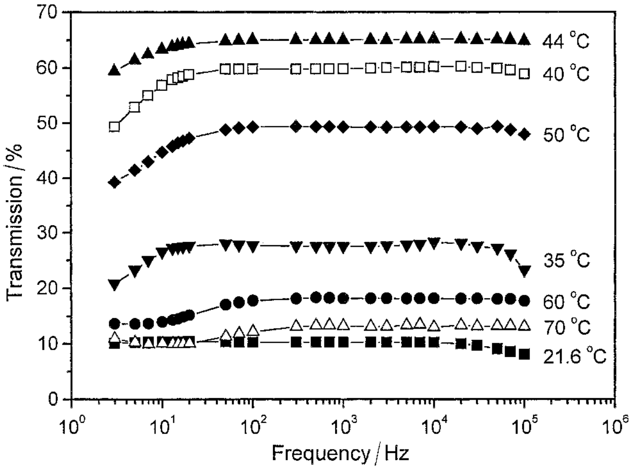

Figure 7. Transmission as a function of frequency at various temperatures for the film with 82.9 wt % TL213. Transmission was measured at an applied voltage of 3 V_{rms}.

field, which reduces the actual voltage across the droplets. Because ionic movements are frozen out at sufficiently high frequencies, we are able to determine from this measurement whether the depolarization field due to ionic movements is the origin of the declining transmission at high temperatures. It transpires that the transmission depends moderately on frequency at low frequencies (3–100 Hz) but insignificantly at higher frequencies up to 100 kHz. The moderate increase of the transmission in the low frequency region indicates that the mobility of ions present in the cell is relatively low. Therefore, it can be concluded that the noticeable depolarization effect due to these ionic motions manifests itself only at frequencies below 100 Hz, regardless of the temperature. It has been observed also that the transition from the conductivity regime to the dielectric regime occurs over the frequency range 20–100 Hz, and that the crossover frequency increases with increasing temperature. However, it should be noted that the temperature at which the transmission peaks are observed is independent of the frequency, as seen clearly in figure 7. This result strongly suggests that movements of pre-existing ions in the PDLC film are not the main source of the decrease in the transmission above 43°C. This reasoning leads to a tentative conclusion that the unusual temperature dependence should be associated with some phenomenon which occurs strongly only at high temperatures. It will be shown later in this section that this phenomenon is closely related to conductivity effects.

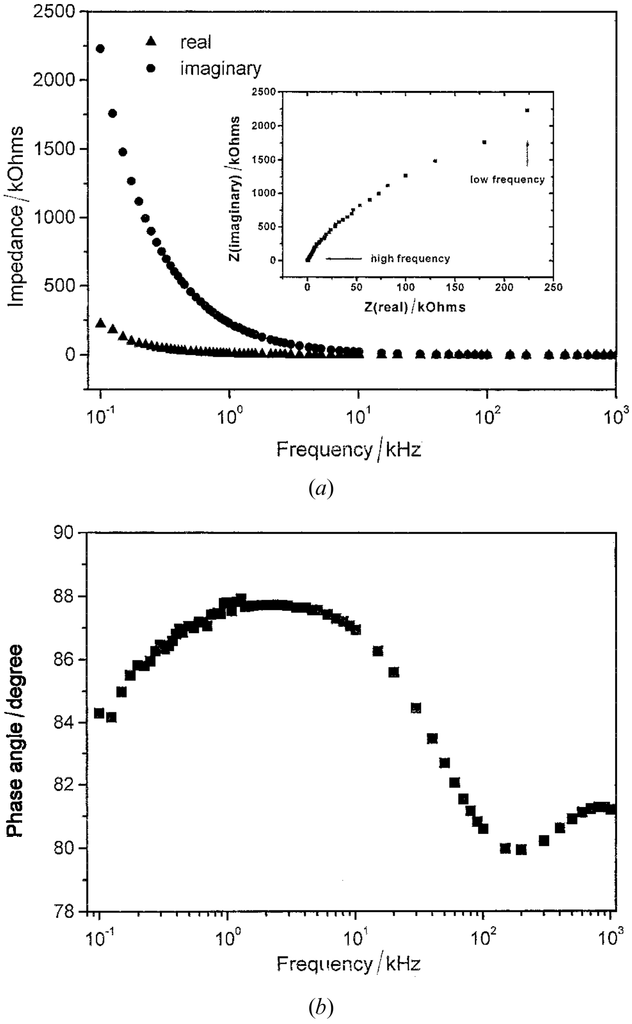

Figure 8. (*a*) Impedance of the cell with 82.9 wt % TL213 as a function of frequency: plot of imaginary part versus real part is in the inset. (*b*) Phase for the cell with 82.9 wt % TL213 as a function of frequency.

Measurement of the frequency-dependent impedance is a powerful method for analysing the electrical properties of PDLC films [25]. The impedance and the phase for the cell containing 82.9 wt % TL213 have been measured at ambient temperature as a function of frequency, see figures 8 (*a*) and 8 (*b*), respectively. A plot of the imaginary part versus the real part is shown in the inset of figure 8 (*a*). An HP vector impedance meter was used for these measurements. One of the ideal equivalent circuits for PDLC films is a three-element model, as shown in figure 9 [6]. This circuit consists of a parallel resistor

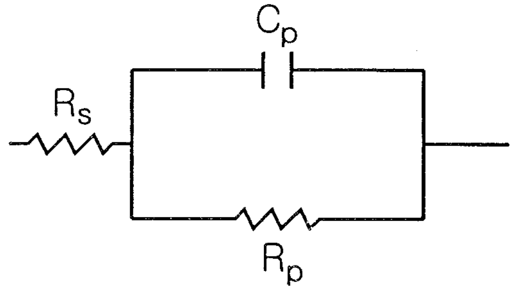

Figure 9. An idealized three-element circuit diagram for PDLC systems.

R_p and a parallel capacitor C_p, which represent the heterogeneous LC/polymer system. The series resistor R_s represents the resistance of the conductive ITO substrate. According to this model, the real and imaginary parts of the impedance are given by equations (5) and (6):

$$Z_{\text{real}} = R_s + \frac{R_p}{1+(\omega R_p C_p)^2} \qquad (5)$$

$$Z_{\text{im}} = -\frac{\omega R_p^2 C_p}{1+(\omega R_p C_p)^2}. \qquad (6)$$

It can be seen from figures 8(*a*) and 8(*b*) that Z_{im} is much larger than Z_{real} over the entire range of frequency, and that the magnitude of the phase angle is in the range 80–88°. It can be deduced from these measurements that the electrical property of the PDLC film is capacitive rather than resistive. When a three-element model is applicable, an impedance-plane plot, such as the inset in figure 8(*a*), contains a semicircular arc centred on the real axis [26]. However, there are many cases in which the three-element model is not able to reproduce accurately the electrical properties of real PDLC films. For example, a considerable deviation from this model has been observed for PVA-based films at low frequencies [6]. This kind of behaviour has been known to result from ionic motions through the system at low frequencies. In our case, a similar deviation was observed only at low frequencies implying that some ions were present in the PDLC film.

We measured the electric current through the PDLC cell at an applied signal of 5 V_{rms} (1 kHz sinusoidal). The experimental results show that the current increases quite rapidly above 43°C, see figure 10. The rapid increase of the electric current is believed to stem from an increase in the free ions dissolved in the LC materials. These ions can originate either from the LC materials or from the polymer components at high temperatures. For instance, it may be possible that the pre-existing free radicals, neutral LC molecules and/or polymer molecules can be dissociated into smaller ions at high temperatures [27]. This dissociation can result in the higher concentration of free ions within the droplets and in turn cause a deterioration in the electro-optical properties of the PDLC film. If these newly created ions produce conductivity effects at high temperatures, the equation (4*b*) is a valid expression for estimating the actual field across a droplet. In this case, E_d lies within the range 0 to $3E_a/2$. Furthermore, if the rapid increase of the electric current results mainly from the corresponding increase in σ_{LC}, then E_d can be less than E_a. These arguments can explain the observation in figure 4 that the peaks are most pronounced in the low voltage region (2–4 V) and gradually become broader and smaller with increasing applied voltage. The threshold switching voltage is in the range 2–4 V, as shown in figures 1 and 2. Thus, small changes in the actual voltage across the droplets are expected to affect the transmission more critically in the low voltage region.

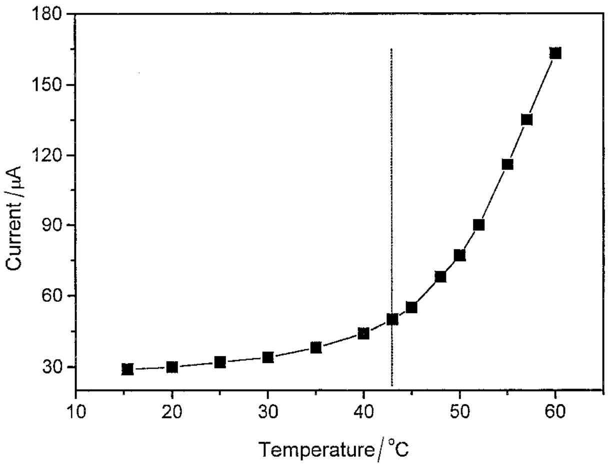

Figure 10. Electric current through the PDLC cell with 82.9 wt% TL213 as a function of temperature at an applied signal of 5 V_{rms} (1 kHz sinusoidal).

4. Conclusions

In this work, the dependence of the electro-optical properties of PDLC films on temperature was studied. An unusual shift of the transmission curves towards higher voltages above 43°C was observed. Microscopic observations of the LC droplets at varying temperatures revealed that the effective voltage across the droplets was reduced with increasing temperature. It is concluded that conductivity effects due to free ions, newly created at high temperatures, could be responsible for the unusual temperature dependence of the transmission.

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