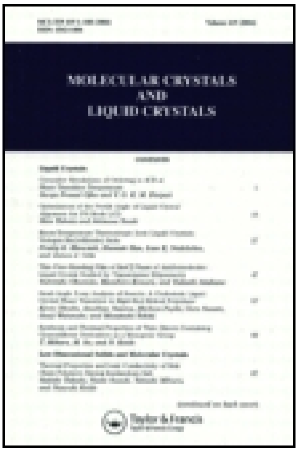

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Dielectric Properties of a Polymer-Dispersed Liquid Crystal Film

D. K. Rout [a] & S. C. Jain [a]
[a] Display Devices Group, National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi, 110012, IndiaPACS No: 77.20 + y, 77.40 +, 77.55 + f, 78.20 Jg

Version of record first published: 24 Sep 2006.

To cite this article: D. K. Rout & S. C. Jain (1992): Dielectric Properties of a Polymer-Dispersed Liquid Crystal Film, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 210:1, 75-81

To link to this article: http://dx.doi.org/10.1080/10587259208030758

Mol. Cryst. Liq. Cryst., 1992, Vol. 210, pp. 75–81
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Dielectric Properties of a Polymer-Dispersed Liquid Crystal Film

D. K. ROUT and S. C. JAIN

*Display Devices Group, National Physical Laboratory, Dr. K. S. Krishnan Marg,
New Delhi-110012, India*

(PACS No: 77.20+y, 77.40+, 77.55+f, 78.20 Jg)

(Received December 14, 1990; in final form June 20, 1991)

Dielectric properties of a polymer-dispersed liquid crystal (PDLC) film comprising of liquid crystal, octyl cyanobiphenyl (K-24) and polymethyl methacrylate (PMMA) are reported as a function of frequency (100 Hz–1.0 MHz) in the temperature range of 25°C to 45°C. A dielectric dispersion in the low frequency region (~1 KHz) was observed while no such dispersion was seen in either pure PMMA or pure K-24. The dispersion is due to Maxwell-Wagner polarization mechanisms. The temperature variation studies show (i) a discontinuous jump in the dielectric permittivity at the nematic-isotropic and smectic-nematic transitions and (ii) also a lowering of the transition temperatures, suggesting some contamination of liquid crystal by the polymer. Simple dielectric theories of composites have been applied to estimate the molecular alignment of liquid crystal (LC) molecules inside the micro-droplets.

I. INTRODUCTION

Polymer-dispersed liquid crystals (PDLCs) are emerging as an important class of composites which are very interesting both from basic as well as application[1–3] points of view. In a PDLC film, a liquid crystal material of positive dielectric anisotropy and large birefringence is imbedded in an isotropic polymer matrix in the form of very fine droplets of micron and sub-micron sizes. The PDLC film is highly scattering, giving rise to a milky white appearance in the 'off' state and becomes transparent on application of an electric field. The electro-optic performance characteristics of such a film, i.e., the threshold electric field and its sharpness, the scattering properties etc. are dependent on a variety of parameters such as the refractive index, dielectric permittivity, conductivity etc. of the polymer as well as of the liquid crystal and on the shape, size and density of the micro-droplets and the molecular alignment inside the droplets.

In the present paper, dielectric properties of a PDLC film are reported as a function of frequency (100 Hz–10 MHz) in the temperature range (25°–45°C). Simple dielectric theories of the composites[4,5] have been applied to estimate the molecular alignment of LC molecules inside the micro-droplets.

II. EXPERIMENTAL

The PDLC film was made using liquid crystal compound K-24 and polymer (PMMA) by a solvent-induced phase separation technique.[6,7] PMMA and K-24 were obtained from M/s Polysciences Inc., USA and M/s B.D.H. Ltd., U.K. respectively and were mixed in the weight ratio of 1:1.5. The thickness of the casted film was measured by a surfometer SF-100 (M/s Planer Industrial Co., U.K.). The PDLC film was sandwiched between patterned conducting glass plates at elevated temperatures under pressure. The dielectric cells for determining the dielectric permittivity of K-24 were made using mylar spacers to control the cell thickness. The necessary planar and homeotropic alignment of the LC molecules for measuring $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ respectively, was promoted by suitable surface treatment of the electrode surfaces. The cell constant was determined by measuring the capacitance of the standard liquids i.e., benzene, carbon tetrachloride and cyclo-hexane etc. The dielectric measurements were carried out by a Hewlett-Packard 4192A Impedence Analyzer. The temperature of the cell was controlled by a water circulator (Julabo HC-40, W. Germany) to an accuracy of ±0.1°C.

III. RESULTS AND DISCUSSIONS

The dielectric properties of pure polymer PMMA, liquid crystal K-24 and PDLC film comprising of PMMA and K-24 in a weight proportion of 1:1.5 have been studied as a function of frequency in the whole liquid crystalline temperature range of K-24. Figure 1 shows the frequency dispersion of the dielectric permittivity, and the dissipation factor (dielectric loss), D of PMMA, K-24 (both $\varepsilon_{\parallel}$ & $\varepsilon_{\perp}$) and PDLC film at room temperature (27°C). It is seen that PMMA does not show much change in the dielectric permittivity up to 1 MHz and shows a very small dielectric loss in the studied frequency range. It is also seen that $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of K-24 do not show any significant variation up to 10 KHz and 50 KHz respectively, and show dispersion only at higher frequencies. The loss parameter D shows an exponential increase beyond 100 KHz and corresponds to dipolar relaxation. In contrast, the dielectric permittivity of the PDLC film shows a considerable decrease with increasing frequency in the low frequency range ($\lesssim$1 KHz), apart from showing a dipolar dispersion beyond 100 KHz. The loss parameter D also shows a small shoulder in the low frequency region, although a complete loss peak could not be seen due to instrumental limitation. The dispersion in the low frequency region may be due to the Maxwell-Wagner polarization mechanisms.[4] In the case of spherical inclusion in a nonconducting medium, the relaxation time τ is given by[4]:

$$\tau = \varepsilon_0 \frac{2\varepsilon_P + \varepsilon_{LC} + V(C_P - C_{LC})}{\sigma_{LC}(1 - V)} \tag{1}$$

where ε_0 is the permittivity of free space $= 8.85 \times 10\,\mathrm{E}\ -12\ \mathrm{F.m^{-1}}$, ε_P (=3.18) and $\bar{\varepsilon}_{LC}$ (=7.8) are the dielectric constants of the polymer and of the liquid crystal

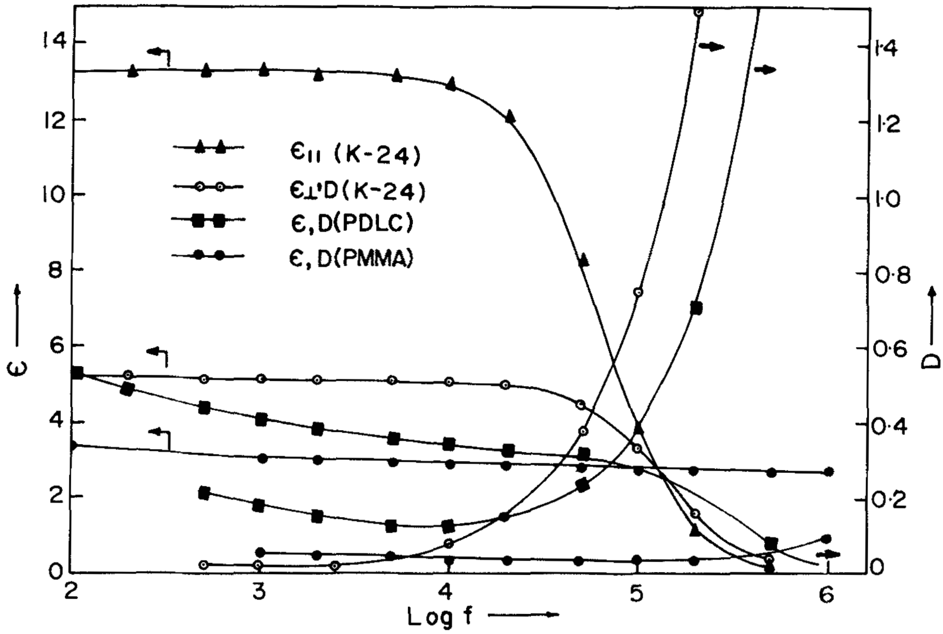

FIGURE 1 Variation in the dielectric permittivity and loss parameter 'D' as a function of frequency of (i) PMMA, (ii) K-24 and (iii) PDLC at 27°C.

respectively, V ($=0.6$) represents the volume fraction of the liquid crystal in the polymer matrix and $\bar{\sigma}_{LC}$, ($=2.6 \times 10^{-8}$ mho/m) its conductivity. Substituting the respective values at 1 KHz (25°), τ was found to be 9.1 × 10 E −3. This value does suggest that the Maxwell-Wagner polarization mechanism should be associated with PDLC in the low frequency region. It may also be mentioned here that the conductivity of the polymer matrix is lower ($\sigma_P = 9.9 \times 10^{-9}$ mho/m) than that of the liquid crystal, which is also a necessary condition for Maxwell-Wagner polarization to occur. The loss peak corressponding to dipolar relaxation in PDLC film is essentially similar to that observed in pure K-24 but it is somewhat shifted to higher frequency.

The dielectric properties of pure PMMA, K-24 and PDLC as a function of temperature have also revealed interesting results. Figure 2 shows the variation in the dielectric constant of PMMA, K-24 and PDLC as a function of temperature. It can be seen that the increase in the dielectric permittivity of PMMA with temperature is small compared to the corresponding increase in K-24 and PDLC film in the nematic temperature range. Dielectric permittivity in PDLC film also shows discontinuous jumps at SmA-N and N-Isotropic transition temperatures. This result clearly shows that the dielectric behaviour of the PDLC film is qualitatively very similar to that of K-24. However, one thing of interest to be noticed here is that the corresponding transition temperatures SmA-N (34°C) and N-I (41°C) observed in pure K-24 are considerably lowered in the case of the PDLC film. The corresponding transition temperatures were 31.5 and 39.5°C respectively (Figure 3). The lowering of the transition temperature is probably caused by the contamination of the liquid crystal by the polymer.

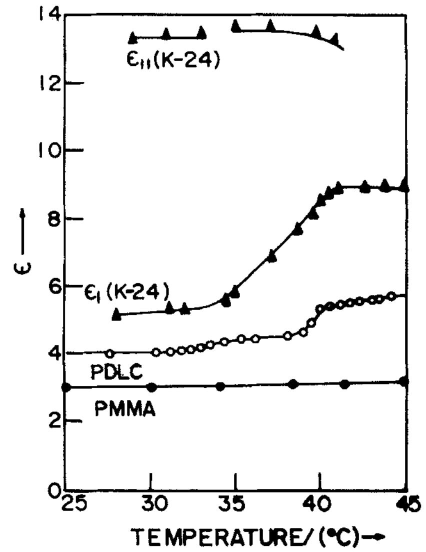

FIGURE 2 Temperature variation of the dielectric permittivity of PMMA, K-24 and PDLC at 1 KHz.

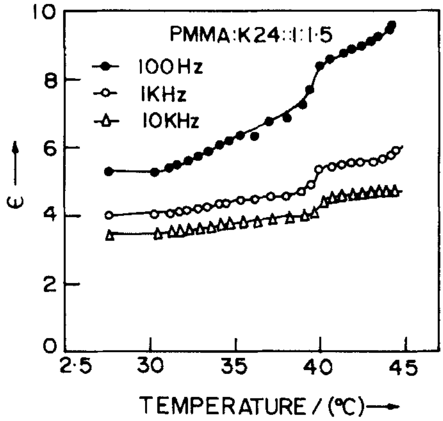

FIGURE 3 Temperature variation of the dielectric permittivity of PDLC at (i) 100 Hz (ii) 1 KHz and (iii) 10 KHz.

An attempt has also been made to estimate the molecular alignment of LC molecules inside the microdroplets by using simple dielectric theories of composites for a heterogeneous system given by Böettcher, Bruggeman[4] and Hashin and Shtrikman[5] respectively. These theories were also used to calculate dielectric constant of PDLCs.[8,10] According to these theories, the dielectric permittivity of a heterogeneous mixture at high enough frequencies where the space-charge effect could be considered to be insignificant is given by

$$\varepsilon_m = \varepsilon_P + 3V\varepsilon_m(\varepsilon_d - \varepsilon_P)/2(\varepsilon_m + \varepsilon_d) \qquad [\text{Böettcher}] \ldots (2)$$

$$1 - V = \frac{\varepsilon_d - \varepsilon_m}{\varepsilon_d - \varepsilon_P} \cdot \left(\frac{\varepsilon_d}{\varepsilon_P}\right)^{1/3} \qquad \text{[Bruggeman]} \ldots (3)$$

$$\varepsilon_m = \varepsilon_P + 3V \cdot \frac{\varepsilon_P(\varepsilon_d - \varepsilon_P)}{\varepsilon_d + 2\varepsilon_P - V(\varepsilon_d - \varepsilon_P)} \qquad \text{[Hashin and Shtrikman]} \ldots (4)$$

where V represents the volume fraction of the dispersed spheres, and ε_d and ε_P represent the dielectric permittivity of the droplets and of the polymer matrix respectively. Dielectric permittivity of the PDLC film was calculated using the above formulae and the measured values of ε_P and ε_d at 1 KHz in smectic, nematic and isotropic phases respectively. For ε_d values $\varepsilon_\perp$, $\varepsilon_\parallel$ and $\bar{\varepsilon}_{av}$ values of K-24 from Figure 2 were taken. Table I shows the measured and calculated values of the dielectric permittivity. It can be seen that there is a satisfactory match between measured and calculated values using $\varepsilon_\perp$, of LC for calculation in the smectic phase, but the difference between them increases in going to nematic and isotropic phases respectively. These results do suggest that the LC molecular alignment inside the droplets is essentially tangential and all the three formulae give similar results. Similar results have also been reported[8,9] using the various formulae mentioned above for a few PDLCs. However, this observation seems to be somewhat strange considering the generally known fact that the molecular orientation inside the droplet is essentially tangential, but the bipolar axis may lie in an out of the plane in case of a spherical droplet. If this were true, then the measured dielectric permittivity of a PDLC should closely match the calculated value, where $\bar{\varepsilon}_{av}$ instead of $\varepsilon_\perp$ is taken for calculation. This discrepancy may be due to inadequacy in the present available theories concerning composites. There are several factors, which have not been taken into account such as (i) modified dielectric permittivity of the polymer due to the plasticizing effect of LC, (ii) change in the volume fraction, V, of liquid crystals due to a finite solubility of LC in the polymer which is found to

TABLE I

Comparison of the dielectric permittivity of a PDLC film with theoretically calculated values using different theories of heterogeneous mixtures

	ε_{mes} at 1 KHz			ε PDLC (Cal.)		
T (°C)	ε_{PMMA}	ε_{LC}	ε_{PDLC}	Boettcher's formula	Bruggeman's formula	Hashin and Shtrikman's formula
25	3.18	5.15($\varepsilon_\perp$)	4.09	4.28	4.28	4.27
		7.85($\bar{\varepsilon}_{av}$)		5.66	5.59	5.52
		13.25($\varepsilon_\parallel$)		8.19	7.81	7.43
35	3.20	5.35($\varepsilon_\perp$)	4.40	4.40	4.39	4.38
		8.03($\bar{\varepsilon}_{av}$)		5.76	5.69	5.61
		13.04($\varepsilon_\parallel$)		8.27	7.80	7.50
42	3.25	8.9($\bar{\varepsilon}_{av}$)	5.5	6.21	6.11	6.0

PDLC = PMMA: K-24::1:1.5.

be ~10–20%[9] (iii) change in dielectric permittivity of LC due to contamination by the polymer, (iv) droplet non-uniformity and coalition of droplets. It is, however, difficult at this stage to account for the change quantitatively for all these factors and this question is still open.

Another important feature of the present studies was the effect of the droplet sizes on the dielectric properties of the PDLC film. The PDLC film, prepared under different cooling rates from the isotropic melt, give rise to very large variation in the droplet sizes. Typically, a film prepared with a slow cooling rate from the isotropic melt showed droplets of a few microns size while the one prepared by rapidly cooling it from the isotropic melt had droplets a few tenths of a micron. Figure 4 shows the dielectric dispersion behaviour of the PDLC film prepared under different cooling conditions. The dielectric permittivity values showed only a very small variation in PDLCs with bigger droplets as well as with smaller droplets and the dispersion characteristics remain essentially the same. This observation clearly indicates that the droplet size does not affect the dielectric properties of the PDLC film in any significant way.

CONCLUSION

A low frequency (~1 KHz) dispersion in PDLC is due to Maxwell-Wagner interfacial polarization mechanisms. In PDLC with high concentration of liquid crystals (1.5 times by weight to that of the polymer), mesophase transitions are also observed but with a reduced temperature. The lowering in transition temperatures is due to the contamination of liquid crystals by the polymer. The dielectric theories developed so far for composites such as a PDLC are inadequate to give information about molecular-orientation inside the micro-droplets.

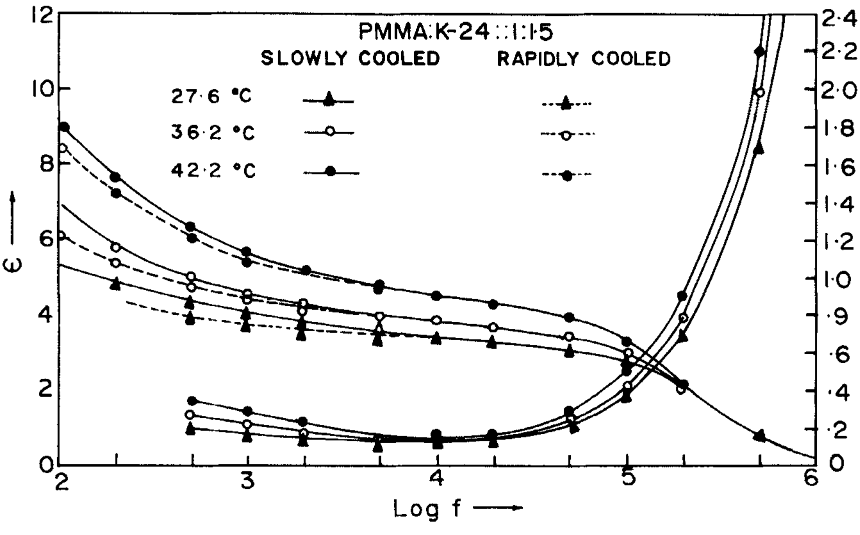

FIGURE 4 Variation in the dielectric permittivity and loss parameter 'D' as a function of frequency of PDLC films in smectic, nematic and isotropic phases prepared under different cooling conditions.

Acknowledgments

The authors are highly thankful to the Director, NPL, for granting permission to publish this work. They are also grateful to Dr. Subhas Chandra for his keen interest in this work. They are also thankful to Dr. S. T. Lakshmi Kumar, Nagendra Beledakare, for useful discussions and computational help.

References

1. Golemme, S. Zumer, D. W. Allender and J. W. Doane, *Phys. Rev. Lett.*, **61**, 26, 2937 (1988).
2. B. G. Wu, J. L. West and J. W. Doane, *J. Appl. Phys.*, **62**, 3925 (1987).
3. G. P. Montgomery Jr. and N. A. Vaz, *Appl. Opt.*, **26**, 738 (1987).
4. L. K. H. Van Beek, 1967, in Progress in Dielectrics. Vol. 7, J. B. Birks, ed., Heywood, London, 69–114.
5. J. Hashin and S. Shtrikman, *J. Appl. Phys.*, **33**, 3125 (1962).
6. J. W. Doane, A. Golemme, J. L. West, J. B. Whitehead Jr. and B. G. Wu, *Mol. Cryst. Liq. Cryst.*, **165**, 511 (1988).
7. S. C. Jain, D. K. Rout and S. Chandra, *Mol. Cryst. Liq. Cryst.*, **188**, 251 (1990).
8. P. S. Drzaic, *Liquid Crystals*, **3**, 1543 (1988); P. S. Drzaic and A. Muller, *Liquid Crystals*, **5**, 1467 (1989).
9. D. K. Rout and S. C. Jain, *Jpn. J. Appl. Phys. Lett.* **30**, 8A (1991).
10. J. Kelly and D. Seekola, SPIE 1257, 17 (1990).