Chapter 7
Polymer Dispersed Liquid Crystals

Shri Singh, Jagdeesh Kumar Srivastava, and Rajendra Kumar Singh

7.1 Introduction: An Overview

During the past three decades, intense studies have been carried out to understand the behaviour of dispersed liquid crystals in various media. One of the most common outcomes related with these dispersion studies on liquid crystals is the polymer dispersed liquid crystals (PDLCs) (Drzaic 1995; Crawford and Zumer 1996; Simoni 1997; Higgins 2000; Dierking 2000, 2003; Vicari 2003; Crawford 2005; Yang and Wu 2006; Dunmur and Sluckin 2010). These systems are interesting from both technical applications and understanding of the behaviour of liquid crystals in a confined environment. Various binary and multi component mixtures of both liquid crystals and polymers with other additives (like dyes, nano particles, etc.) have been used to improve its technological applications. In general, PDLCs are the micrometer-sized birefringent liquid crystalline droplets, dispersed in an optically transparent and uniform polymer matrix having spatially varying refractive index and efficient light-scattering properties. It is useful in the study of problems related with phase separation, miscibility, droplet configuration, surface anchoring, etc. It is also useful in various device development applications like smart windows, light shutters, modulators, sensors, optical switches, holographic films and most interestingly the display devices.

Recently, important results on the dispersion studies of liquid crystals in photo-aligned materials (Yaroshchuk and Reznikov 2012), adhesives (Zou and Fang 2011), smart windows (Cupelli et al. 2009) and conducting polymers (Buyuktanir et al. 2006; Kim et al. 2008), etc., have been reported. Self-assembling of liquid crystalline materials in pyroelectric substrates (Sheraw et al. 2002; Merola et al. 2012), phosphonium type zwitterions (Ueda et al. 2011) and phase

S. Singh, Ph.D. (✉) • J.K. Srivastava, Ph.D. • R.K. Singh, Ph.D.
Department of Physics, Faculty of Science, Banaras Hindu University,
Varanasi, Uttar Pradesh 221005, India
e-mail: srisingh23@gmail.com; jagdish.bhu@gmail.com; rajendrasingh.bhu@gmail.com

segregated liquid crystal gels (Hikmet 1992; Guymon et al. 1997; Kato 2002) are also of much interest.

Dispersion of particles in a host medium is the part of our everyday life and an important area for fundamental research. In wider sense, dispersion may be in the form of emulsion, colloidal suspension, aerosols, etc. In emulsion, surfactant-coated liquid droplets are dispersed in a fluid environment. Colloidal suspensions are observed for the dispersion of solid particles in the fluid medium and aerosol with fluid or solid particles floating in a gaseous phase. The physics of colloidal dispersions in nematic liquid crystals has been discussed in detail by Stark (Stark 2001). Dispersion studies on liquid crystals give rise to an important area of scientific and technological developments. A great deal of interesting physics is associated with the liquid crystalline materials confined into small cavities. It leads to the observed changes in the mesoscopic properties of liquid crystalline materials in confined geometry as compared to their bulk counter parts (Golemme et al. 1988a). Consequently, the liquid crystal dispersion has been the subject of continuous attention in the recent past (Wu 1986; Simoni et al. 1993; Sutherland et al. 1994; Drzaic 1995; Crawford and Zumer 1996; Hourri et al. 2001; Yamamoto 2001; Iannacchione et al. 2003; Leheny et al. 2003; Vicari 2003; Stannarius and Kremer 2004; Pasini et al. 2003; Spicer 2005; Cristaldi et al. 2009).

Dispersion study of liquid crystals in polymers constitutes an important area because of its wide applicability in various scientific (Drzaic 1995; Crawford and Zumer 1996; Mucha 2003; Pasini et al. 2003) and device development applications (Klosowicz and Zmija 1995; Simoni 1997; Vicari 2003; Crawford 2005; Lowe and Kriss 2006; Yang and Wu 2006). In a polymer matrix, liquid crystals may exist as a discrete droplet (Chien et al. 1992; Roussel et al. 2002; Hoppe et al. 2003), an interpenetrating network with the polymer (Ciferri 1991; Collyer 1993; Carfagna 1994; Zumer et al. 1995; Collings and Hird 1997; Dierking 2000; Wang and Zohu 2004), or something in-between (Demus and Richter 1978; Demus et al. 1999; Serbutoviez et al. 1996; Benmouna et al. 1999, 2000; Boussoualem et al. 2004; Xie et al. 2005). Confinement of liquid crystals in micrometer size polymer cavities of complex shapes is generally termed as polymer dispersed liquid crystals (PDLCs). Depending upon the nature and compositions of both liquid crystals and polymers some other sub classified terms like polymer network liquid crystal (PNLC), polymer dispersed ferroelectric liquid crystal (PDFLC), polymer stabilized ferro-electric liquid crystal (PSFLC), holographic PDLC (HPDLC), etc., are also common to PDLCs. Starting with the earlier work on PDLCs by Fergason (1984, 1985), Drzaic (1986) and Doane et al. (1986, 1987), presently, a large number of groups are working in the field of PDLCs. Different properties of PDLCs like droplet morphology, birefringence, light scattering, flexibility, self-supportability and electro-optical properties make them interesting for various display applications. As a result much of the works on PDLCs aim to optimize its suitability for display applications by incorporating new modes for displays.

In spite of its strong device development applicability, PDLCs are also interesting from scientific point of view. Several fundamental studies related with mixing and phase separation of liquid crystals with polymers (Smith and Vaz 1988; Smith

1990, 1993a, b), their thermal characterizations (Smith et al. 1992; Russell et al. 1995), phase behavior (Chiu and Kyu 1995, 1998; Riccardi et al. 1998a, b; Benmouna et al. 1998), phase stability (Dorgan 1991, 1995; Shen and Kyu 1995; Riccardi et al. 1998a, b), phase diagrams and morphology (Amundson et al. 1997; Roussel et al. 2000), anchoring and droplet deformation using NMR techniques (Crawford et al. 1991b; Iannacchione et al. 1997; Ambrozic et al. 1997; Vilfan et al. 1999a, b), different computer simulations to investigate droplet configurations (Erdmann et al. 1990; Berggren et al. 1994; Priezjev and Pelcivits 2000; Springer and Higgins 2000), electro-optical properties of PDLCs (LeGrange et al. 1997; Jadzyn et al. 1999; Nicoletta et al. 2000; Smith et al. 2000), and many more other investigations have been carried out.

Thrust remains continued in the current millennium as well, which results in a large number of articles covering both the experimental and theoretical aspects of PDLCs. Matsuyama (2010) has discussed the theory of phase separation in the binary mixtures of low molecular weight liquid crystal and a rod like polymer using mean field theory. Both the experimental and simulation studies have been carried out to investigate phase equilibrium and growth morphology for the mixture of polystyrene and cyanobiphenyl (Soule et al. 2009). PDLCs with micrometer size droplets useful for diffractive optics have been investigated by Hadjichristov et al. (2009). Phase separation kinetics of polymer dispersed liquid crystals confined between two parallel walls using time dependent Ginzburg–Landau Model has been discussed by Xia et al. (2006). Expression for topological point defects in nematic liquid crystals (Kleman and Lavrentovich 2006) and optical phase shift of light propagating through LC droplets in PDLCs (Dick and Loiko 2004) have also been highlighted.

Monte Carlo and molecular dynamics simulations have been carried out to investigate the different properties of PDLCs. Phase behavior of nematogen (Almarza et al. 2010), surface induced ordering and influence of director fluctuation in PDLCs, using simulated NMR spectra (Amimori et al. 2005; Preeti et al. 2009), nematic cells with defect patterns (Backer et al. 2008), computer simulations of nematic liquid crystal tactoids (Bates 2003), director configuration in confined nematics (Priezjev and Pelcivits 2000), opto-mechanical and other light scattering properties of stretched PDLC films (Zumer and Doane 1986; Kiselev et al. 2004; Amimori et al. 2003) and molecular dynamic simulation studies on LCs and PDLCs (Care and Cleaver 2005; Jeon et al. 2007; Wilson 2007; Zheng et al. 2008) are of much interest.

Performance of PDLC based devices has been improved by using different mixtures of liquid crystals, polymers and other additives. Many studies reveal the importance of electro-optical properties of PDLCs using gold nano particles (Hinjosa and Sharma 2010), reverse mode operation in PDLCs (Cupelli et al. 2011), reconfigurable LC droplets (Ren et al. 2009), electrowetting (Fan et al. 2009), electro-optical switching of HPDLC diffraction gratings using SiO_2 and clay as nanocomponent (Busbee et al. 2009; Pavani et al. 2009). For flexible display devices, PDLCs with conducting polymers (Sheraw et al. 2002; Roussel et al. 2003; Ebru et al. 2006; Kim et al. 2008) and PEO-based liquid crystalline

block copolymer (Zhou et al. 2011) have been investigated. In past few years the thermal, morphological, phase behavior and electro-optical properties of PDLCs using different polymer matrices have been studied by many research groups (Malik et al. 2003, 2008; Malik and Raina 2004; Chen and Shanks 2007; Kumar and Raina 2007; Deshmukh and Malik 2008; Ganesan et al. 2009; Meng et al. 2010; Perju et al. 2011; Dzhons et al. 2011; Shanks and Staszczyk 2012; Srivastava et al. 2011, 2012; Song et al. 2012a, b).

Purpose of the present chapter is to provide self-contained overview of the polymer dispersed liquid crystals for attracting the interest of novice readers. An attempt is also made to generate curiosity among the established workers by making them familiar with some of the very recent development in the area of PDLCs. The present chapter provides a comprehensive view on different aspects of PDLCs viz., methods for preparation; basic techniques for characterization; their morphological, electro-optical and temporal behavior; various applications, and, the basic theoretical understanding of miscibility and phase related phenomenon. Some non-conventional methods for the preparation of PDLC films, different director configuration and their *inter-se* transformations within the LC droplets and future perspectives have also been discussed.

7.2 Polymer Dispersed Liquid Crystal (PDLC) Films

In their most common form, a PDLC consists of micron-sized birefriengent liquid crystalline droplets, dispersed uniformly in an optically active and transparent polymer matrix, having spatially varying refractive index and efficient light-scattering properties. The light scattering may be switched on by applying an electric field across the film which reorients the molecular directors in nematic droplets to match their ordinary refractive index (η_o) with the refractive index of the polymer (η_p), thereby, making the film transparent. PDLC films are prepared with the aim to couple the peculiar mechanical properties of a polymeric film (flexibility and high mechanical resistance) and the peculiar electro-optical properties of LCs (electrically controllable high optical anisotropy). In PDLCs, confinement of liquid crystals into small cavities dominates over the bulk properties of liquid crystals (Parmar and Singh 1992; Parmar and Holmes 1993; Shen and Kyu 1995).

The microscopic structural arrangement of PDLCs itself is very complex, but in simplest form it can be sketched as an optically non-absorbing inhomogeneous material composed of an isotropic solid phase (i.e., the polymer), containing almost spherical droplets filled with an anisotropic liquid (i.e., a nematic liquid crystal). In PDLCs, both polymer and liquid crystal have slightly different refractive index values. When no field is applied to the film, director of the nematic droplets has no preferred orientation with respect to the plane of the film. In this case, the difference between refractive indices of polymer and liquid crystal results in the scattering of incident light. Therefore, film becomes opaque. On the other hand, when electric field is applied to the film it tends to reorient nematic liquid crystal droplets in such a
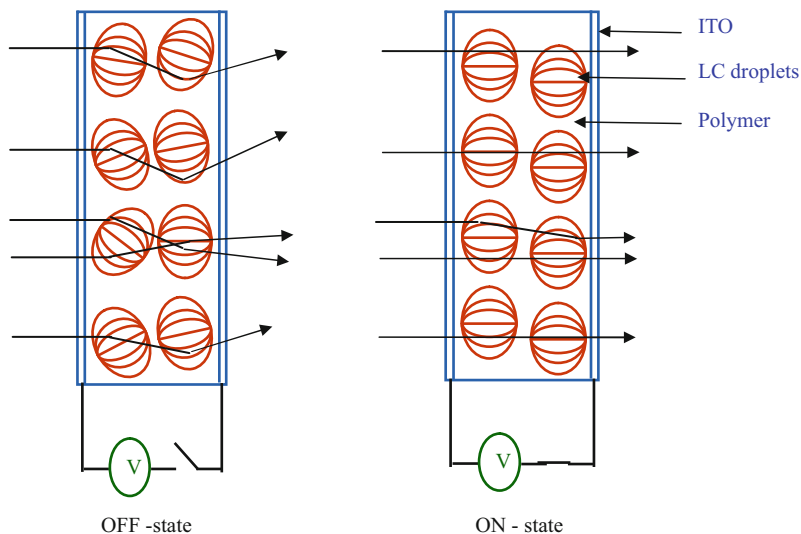
Fig. 7.1 Operating principle of a common PDLC device. (**a**) OFF-state, (**b**) ON-state

manner that the director becomes parallel to the field (or otherwise, perpendicular to the plane of the film). In this case, ordinary refractive index (η_o) component of liquid crystal matches with refractive index of the polymer (η_p). Thus, light incident on normal to the film, passes through it without being scattered and film becomes transparent. The operating principal of a common PDLC device is shown in Fig. 7.1.

There are certain aspects common to all PDLC films which need to be explored properly for optimized utility of a particular PDLC film in typical applications. These include film thickness; liquid crystal droplet size and shape; refractive indices, solubility/miscibility behavior, etc. of the constituting liquid crystals and polymers.

Both the operating voltage and light scattering properties of PDLCs depend strongly on the PDLC *film thickness* (Drzaic 1995). Usually it is controlled by using spacers of known dimension. Spacer may be a thin polymer film, Mylar sheet, glass and plastic rods (or spheres), etc. PDLC film thickness is measured conveniently by interferometry. In interference pattern, fringes of different series are observed due to phase shift of the light reflected from the front and rear surfaces of the film. Light reflected from rear surface, suffers a phase shift in proportion to the distance travelled inside the film (i.e., twice the film thickness). Once these fringes are identified, PDLC film thickness can also be obtained.

The *droplets shape, size and distribution* influence strongly the scattering, reorientation and electro-optical properties of the PDLC films. It is usually determined by scanning electron microscopy after removing liquid crystals from polymer network using suitable solvents (Havens et al. 1990; Vaz et al. 1991). In some cases it can also be determined by the image analysis of the morphologies obtained from optical microscopy (Golovataya et al. 1990). One direct method to obtain the

average droplet size involves counting droplets of different sizes in POM images (Hadjichristov et al. 2009). In indirect methods, light scattering and electro-optical properties can also be used to estimate the average droplet size (Lackner et al. 1989; Vaz et al. 1991).

Issues related with *refractive indices and solubility/miscibility* behavior of liquid crystal and polymer complicate the analysis and optimization of PDLC devices. In many of the applications it is mandatory to minimize the haziness of the PDLC films. Haziness effect is minimized by a suitable choice of liquid crystal and polymer constituents with closely matched values of refractive index components (Drzaic 1995). Further, due to *solubility/miscibility* of liquid crystal in polymer, various properties of the PDLC films like transparency, dielectric constant, conductivity and mechanical stability get changed (Fergason 1985; Drzaic 1986; Doane et al. 1986; Golemme et al. 1988a, b; Simoni et al. 1992b; Crawford and Zumer 1996; Mei and Higgins 1998; Mertelj and Copic 1998). Studies on the solubility limit of liquid crystals in different polymer matrices can also be useful in developing an idea about the droplet morphology and their dispersion in polymer matrices (Smith and Vaz 1988; Smith 1990, 1993a, b; Smith et al. 1992; Srivastava et al. 2011).

The solubility parameters or rather the difference in solubility parameter components are significant in determining the solubility of a system. The term solubility parameter was first used by Hildebrand and Scott (Hildebrand and Scott 1950, 1962) and is defined as the square root of the cohesive energy density,

$$\delta = \left(\frac{E_{coh}}{V}\right)^{\frac{1}{2}} \tag{7.1}$$

and

$$E_{coh} = \Delta U = \Delta H - P\Delta V \tag{7.2}$$

where, E_{coh} is the cohesive energy and V the molar volume of the substance.

Regular improvements in the studies related with solubility parameter components have been made by several groups (Burrell 1957, 1962, 1972; Blanks and Prausnitz 1964; Hansen 1967a, b, c; Hansen and Skaarup 1967; Hansen and Beerbower 1971; Gardon and Teas 1976; Hoftyzer and Krevelen 1976; Hoy 1970, 1985, 1989; Barton 1985, 1991). Presently, the solubility parameter approach proposed by Hansen (2007) with the help of computer programme data is widely in use. In this approach three distinct solubility parameter components representing dispersion (D), polar (P) and hydrogen bond (H) interactions are used (Hansen 2007) and the total cohesive energy (E_{coh}) is written as the sum of the individual energy terms,

$$E_{coh} = E_D + E_P + E_H \tag{7.3}$$

Its division by the molar volume (V) gives the square of the total (or Hildebrand) solubility parameter as the sum of the squares of the Hansen solubility parameter components related with dispersion (D), polar (P), and hydrogen bond interaction (H).

$$\frac{E}{V} = \frac{E_D}{V} + \frac{E_P}{V} + \frac{E_H}{V} \tag{7.4}$$

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{7.5}$$

Analytically, solubility parameter components are determined by using the methods developed by (i) Hoftyzer and Krevelen (1976) and Hoy (1985, 1989) and then taking the average of the two for a fair estimation. Specific group contribution to the molar volume has been reported by Fedors (1974). Detailed studies related with solubility parameter and group contribution are reported in literature (Krevelen and Nijenhuis 2009). Here we provide only a brief description of the methods.

– **Method of Hoftyzer and Van Krevelen**: It predicts solubility parameter components from group contributions using relations (Hoftyzer and Krevelen 1976),

$$\delta_D = \frac{\sum F_{Di}}{V}; \;\; \delta_P = \frac{\sqrt{\sum F_{Pi}^2}}{V}; \;\; \delta_H = \sqrt{\frac{\sum E_{Hi}}{V}} \tag{7.6}$$

where, F_{Di} and F_{Pi} are, respectively, the group contributions due to dispersion and polar components of the molar attraction function and E_{Hi} is the contribution due to hydrogen bonding forces to the cohesive energy of each structural group and V is the molar volume of the substance.

– **Method of Hoy**: In many respects this method is different from that of Hoftyzer and Krevelen (1976) and makes use of a number of equations as given in (7.7). It contains four additive molar functions, a number of auxiliary equations and the final expressions for the solubility parameter δ_t and its components, total group contributions F_t, group contribution due to polar components F_P and the molecular volume V of the substance.

Additive molar functions	Auxiliary equations	δ_t and its components	
$F_t = \sum N_i F_{t,i}$	$\alpha(P) = \dfrac{777 \Delta_T^{(P)}}{V}$	$\delta_t = \dfrac{(F_i + B)}{V}$, $B = 277$	
$F_p = \sum N_i F_{p,i}$	$n = \dfrac{0.5}{\Delta_T^{(P)}}$	$\delta_P = \delta_t \left(\dfrac{1}{\alpha} \dfrac{F_p}{F_t + B} \right)^{\frac{1}{2}}$	(7.7)
$V = \sum N_i V_i$	---	$\delta_H = \delta_t \left[(\alpha - 1)/\alpha \right]^{\frac{1}{2}}$	
$\Delta_T^{(P)} = \sum N_i \Delta_{T,i}^{(P)}$	---	$\delta_D = \left(\delta_t^2 - \delta_P^2 - \delta_H^2 \right)^{\frac{1}{2}}$	

$\Delta_T^{(P)}$ is the Lydersen correction for non-ideality, derived by Hoy (1985, 1989) and is to be multiplied by 2/3 for bi, tri and tetra-valent groups in the saturated ring.

7.3   Methods for Preparation of PDLC Films

Formation of PDLC films starts with coating of a fluid system as a thin film (which contains both the polymer and the liquid crystals) and then causes it to solidify. Over the years, a number of ways have been developed for the formation of PDLCs films. However, all these fall into two general categories (i) the microencapsulation and (ii) the phase separation methods. Recipes for the preparation of PDLCs are documented well in the literature (Drzaic 1995; Higgins 2000; Mucha 2003; Vicari 2003). We mention here, briefly, these two methods and a few nonconventional methods developed recently in the following sub sections. Depending upon the specific requirements of PDLC properties, various combinations of these methods are adopted in practice.

7.3.1   Microencapsulation Method

It is the simplest method for preparing PDLC films (Fergason 1984, 1985). In it, first, an emulsion of water-soluble polymer and water insoluble liquid crystal is prepared by rapid stirring. The PDLC films are formed using spin-coating or simple deposition of an appropriate amount on a glass substrate (preferably coated with indium tin oxide, i.e., ITO) and letting the water to evaporate normally. In most of the general cases, water soluble polymer polyvinylalcohol (PVA) is used with different mesogenic materials. Because of the insolubility of liquid crystals in aqueous media, in microencapsulation, phase separation is achieved automatically. As a result, films produced in this way are reproducible and problem related with the plasticisation of polymer is not observed. However, hygroscopic nature of polymers sensibly reduces its abilities.

7.3.2   Phase Separation Methods

In this technique, as developed by Doane and co-workers (1986, 1987), the PDLC films are formed by a homogeneous solution of liquid crystal and polymer. During the solidification of homogenous solution most of the liquid crystal molecules are expelled from the polymer via various phase separation mechanism and liquid crystal molecules aggregate in droplets which remain embedded in the polymer film. There are various ways to implement this method as described below.

7.3.2.1   Polymerisation Induced Phase Separation (PIPS) Method

In PIPS method, the polymerisation is induced by an exposure of a homogeneous solution of liquid crystal and low molecular weight monomer or oligomer to heat, light or radiation. During the polymerisation, solubility of polymer and liquid crystal decreases and phase separation occurs. Due to phase separation, polymer chain forms a matrix surrounding discrete liquid crystalline domains. The PDLC films formed by PIPS method are quite durable, leading to good stability of PDLC based devices. One concern in the PIPS process is that it is sensitive to temperature, light intensity of the photo curing system, presence of impurity, solubility characteristic and molecular weight of the starting materials. Small variation in these parameters leads to different morphologies of the films with different electro-optical responses.

7.3.2.2   Solvent Induced Phase Separation (SIPS) Method

The SIPS is a process in which mutually soluble polymers and liquid crystals are mixed with an organic solvent to form a single-phase mixture. Evaporation of the solvent from the mixture causes phase separation of the polymer and liquid crystalline phases. Due to mutual solubility of liquid crystal and polymer, significant plasticization of polymers is observed. Although the plasticization may cause problems in some applications, it can also be useful in increasing the mouldability and flexibility of the film.

7.3.2.3   Thermal Induced Phase Separation (TIPS) Method

It refers to the mixing of liquid crystals in a thermoplastic melt at high temperature. On cooling the mixture, solidification of polymer induces phase separation of liquid crystals. This method is useful where a prefabricated cell is to be filled with the PDLC material. Further moderate solubility of liquid crystals in polymers leads to the plasticization of the polymers. As a result, a comparative reduction in both the number and size of droplets is observed.

7.3.3   Some Other Non-conventional Methods

Apart from the afore-mentioned conventional approaches, recently, several non conventional approaches have also been developed for the preparation of PDLCs films.

Kumano et al. (2011) have studied the multicolor PDLCs formed by *impregnation* of two liquid crystals 4-cyano-4′-pentylbiphenyl (5CB) and 4-(trans-4-pentyl-cyclohexyl)

benzonitrile (PCH5) in the porous networks composed of N-methyl methacrylamide (MMAA) and N,N′-methylene-bis-acrylamide(BIS) as the monomer and cross-linker, respectively. This material changes its structural color covering the whole *visible region* in response to temperature by means of changes in both the diffraction properties and the wavelength dispersions of its refractive indices. At lower temperature, the randomly arranged LC in porous polymer network gives a translucent or milky appearance due to the scattering of the applied white light. However, at higher temperatures when LC reaches at isotropic state, a particular wavelength of light can predominantly be transmitted through the composite material at which the two wavelength dependent dispersion curves for the porous polymer network and LC intersect. Moreover, the point of intersection of the two wavelength dependent dispersion curves varies with temperature. As a result, the composite material exhibits bright coloration and also reveals a change in color in response to temperature. In addition, the structural color of this system may also be tuned by the application of electric field.

In another approach, Zou and Fang (2011) have used PlatSil Gel-10 (a platinum cure silicone kit) and 5CB to develop a free standing *adhesive PDLC film* and studied the change in its LC director configuration on different substrates. The unique feature of the adhesive PDLC film is that its structural and orientational patterns can be printed directly on different substrates by combining soft lithography with cohesive mechanical failure. In the printed PDLC films, director configuration of the dispersed 5CB droplets gets changed by change in the nature of the substrate surfaces. On the glass substrate, phase separation of 5CB from PlatSil Gel-10 shows radial configuration with maltese type crosses. A freestanding PDLC film is formed by peeling it from the glass substrate. When this freestanding film is placed on a rubbed polyimide coated glass substrate it generates parallel alignment of liquid crystal along the rubbing direction and again switches back to radial configuration after peeling out from the polyimide surface. When the film is placed on the adhesive side of 3M tape, the initial radial configuration of 5CB droplet gradually becomes parallel. This radial to vertical configuration is reversible for peeling off the films from 3M tape. Further, the LC droplets remain in the radial configuration when the film is placed on the non-adhesive side of 3M tape. Switching between radial and parallel configurations is due to strong adhesion of the PDLC film which makes an interfacial contact between polymer surface and PDLC film (De Gennes and Prost 1993).

Reversible fragmentation and self-assembling of liquid crystal droplets on *functionalized pyroelectric substrate* have also been reported by Merola et al. (2012). They have used 6CHBT and lithium niobate (LN) as liquid crystalline material and pyroelectric substrates, respectively. Initially, LN is functionalized in various ferroelectric domains by micro-engineering and then its surface is covered by a film of hydrophobic polymer i.e., polydimethylsiloxane (PDMS). Due to hydrophobic (i.e., non-wetting) nature of PDMS when a nematic liquid crystal (6CHBT) comes in contact with PDMS substrate it is difficult to obtain a homogeneous thin layer of 6CHBT. Instead, due to thermodynamic instability, 6CHBT arranges itself in drops with a relatively large contact angle. In this case various
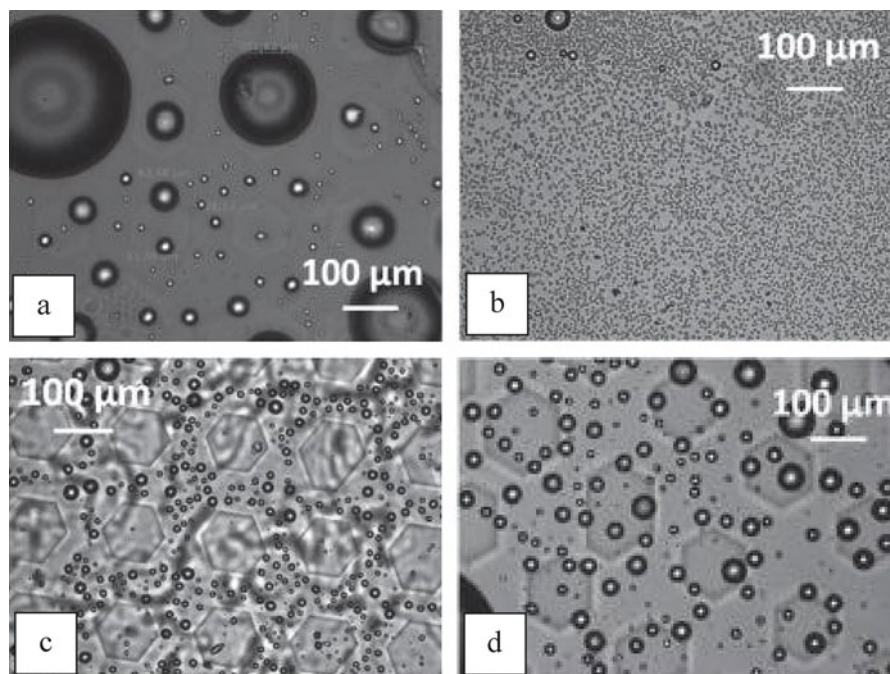
Fig. 7.2 Temporal evolution of nematic liquid crystal (6CHBT) in contact with fabricated PDMS substrate (**a**) scattered LC drops on the substrate before heating, (**b**) fragmented LC droplets after heating at 90 ° C, (**c**) with LN hexagonal domains after 2 h from the beginning of cooling, (**d**) coalesced LC drops on the substrate after some days at room temperature (Reprinted with permission from Adv. Funct. Mater., 2012, **22**, 3267–3272. ©2012, John Wiley and Sons, Merola et al. 2012. Figure 3a, b, d and g)

geometrical structures of LN wafer, being present below the PDMS layers are capable to drive these small droplets. Due to change in the geometry of the LN substrate (i.e., the change in pyro-electrophoretic effect), fragmentation of LC droplets into smaller ones, their migration to the different regions of the sample, coalescence in bigger drops with the possibility of new fragmentation, matrix arrangement and lens effects, etc., have been observed. This study provides completely a new approach to manipulate liquid crystal by pyroelectric effect where the strong electric field generated brought a thermal stimulus which allows to manipulate liquid crystals in 2D on a substrate (Fig. 7.2).

The *holographic gratings* POLICRYPS and POLIPHEM have been proposed to realize a channel structure in which the polymer and LC molecules are almost completely phase separated. Consequently, very high diffraction efficiencies and time response in microseconds were achieved (Caputo et al. 2004). Pavani et al. (2009) have developed a PDLC material to record holographic diffraction gratings. They have used a PDLC layer consisting of monomers (N,N-'-methylenebisacrylamide and n-vinyl-2-pyrrolidinone), photo initiator

(erythrosine B, triethanolamine (TEA)) and LCs (E7) and exposed it to an optical interference pattern. Solidification of polymer through PIPS process under modulated refractive index pattern leads to the development of holographic PDLC gratings with spatially periodic and alternating polymer-LC rich planes.

Through a careful selection of LC, polymer, initiator and other organic additives, switching speed and other optical properties of HPDLCs can be optimized for a given application. Busbee et al. (2009) have demonstrated the incorporation of high volume fractions of chemically *functionalized silica nanoparticle* into electrically switchable HPDLCs with sub-micrometer lattice constants. They have used pentyltriethoxysilane (PTES) and methacryloxypropyl-trimethoxysilane (MPTMS) to get functionalized nanoparticles. Due to chemical functionalization, silica nanoparticles are not sequestered into the liquid crystal but it covalently copolymerizes with the acrylate monomer and do not aggregate. Relatively large change in the electro-optical properties of PDLCs films as an effect of *gold nanoparticles* have been studied by Hinjosa and Sharma (2010). Due to inclusion of small concentration of nanoparticles local electric field is buildup in PDLC. It lowers the threshold voltage needed to switch on the electric field, increases optical transmission at certain voltage and influence the frequency response of PDLCs.

Use of *conducting polymer* poly(3,4-ethylenedioxy thiophene): p-toluene sulfonate (PEDOT:PTS) as electrodes in PDLCs have demonstrated a better electrical performance and light transmittance in similar devices using indium tin oxide as electrodes(Kim et al. 2008). Moreover, use of conductive polymers as electrode layer provides additional flexibility for PDLC device fabrication. Vapor-phase deposited polymerization technique was used for preparing ultrathin layer of PEDOT:PTS conducting layer on polyethylene terephthalate (PET) substrate in the presence of 'iron (III) p-tolune sulfonate (PTS)' solution. Iron (III) salt works as an oxidant for polymerization of PEDOT:PTS on the PET substrate and also provides dopant ions for the conductivity of the polymers. Fabrication of organic thin-film transistor (OTFT) driven PDLC on flexible polymer substrate polyethylene naphthalate film have also been reported (Sheraw et al. 2002). Uses of other conducting polymers such as polyacetylene, polyaniline, polypyrrole, polythiophene, etc., in flexible displays have also been reported (Groenendaal and Gevaert 2005).

7.4   Techniques for Characterization of PDLC Films

With the development of PDLCs, during the past three decades, several experimental techniques have been used to characterize its thermal, morphological and electro-optical behavior. Efforts have also been made to investigate various physical problems related with the phase separation, miscibility behavior, droplet configuration, surface anchoring, etc. Although the description of various characterization techniques used for PDLCs is well documented, for the awareness of novice readers a brief description about some of them is given in the following subsections.

7.4.1 Differential Scanning Calorimetric (DSC) and Thermogravimetric (TGA) Analyses

The DSC is one of the most powerful tools to study the phase transitions occurring in the material. In PDLCs, it is used to investigate the thermal behavior and different mesophase crystallization, melting and glass transition temperature (Hatakeyama and Liu 1998; Cheng 2002; Hohne et al. 2003; Reading and Hourston 2006). Whenever, phase transition occurs, heat is either evolved (exothermic) or absorbed (endothermic) by the material. DSC measures this heat difference through a controlled temperature programme by comparing the energy inputs between the sample and the reference pans as a function of temperature or time. The exact phase transition temperature of the material is determined as the peak of transition which results due to change in the heat of the sample pan as compared with the reference pan. Depending upon the method of measurement, two types of DSC instruments, i.e., heat-flux DSC (Gmelin 1997) and power-compensation DSC (Menczel and Leslie 1990; Menczel and Prime 2009; Schick and Hohne 1991) are in common use.

Thermogravimetric analysis (TGA) is used effectively for quantitative analysis of thermal reactions which are accompanied by mass change. For example, evaporation, decomposition, gas absorption, desorption, dehydration, etc. It is also used to determine the thermal stability of the materials. For TGA investigations, material is subjected either to a constant heating rate (dynamic measurement) or a constant temperature (isothermal measurement) or a non-linear temperature measurement under inert atmosphere. TGA measurements are usually displayed by a curve in which the mass of the material is plotted against temperature and/or time. The first derivative of the TGA curve with respect to temperature or time shows the rate at which the mass changes and is known as the differential thermo gravimetric analysis (DTGA) curve. The basic instrumental requirement for thermogravimetry is a precision balance with a furnace programmed for a linear rise of temperature with time.

7.4.2 Polarization Optical Microscopy (POM)

Polarization optical microscopy is one of the most popular and familiar tools to investigate the morphological changes observed in these materials (Fayolle et al. 1979; Crawford et al. 1991c; Jain and Rout 1991; Kitzerow and Crooker 1993; Lovinger et al. 1994; Amundson 1996; Mirau and Srinivasarao 1997; Yamaguchi et al. 1998; Natarajan et al. 1997; Drzaic and Muller 1989; Magagnini et al. 1999; Coleman et al. 2003; Formentin et al. 2008; Galyametdinov et al. 2008). It provides information not only about the various mesophases present in the material but also about the changes observed in their textures when confined to certain geometry. Morphological changes in the films are observed as a function of temperature, voltage and other physical parameters. When the films are kept in the

path of the light beam crossed with polarizers, birefringent LC droplets alter the polarization state of light passing through them. This alteration results as an increase in the optical power transmitted through the microscope. The distinctive microscopic patterns provide proper information about the local liquid crystal orientation, their overall configuration and mode of anchoring (i.e., homogeneous or homeotropic) at the polymer interface. Depending upon the specific requirement of the material POM can be operated in transmitted or incident light modes.

7.4.3   X-ray Diffraction (XRD)

The X-ray diffraction technique (XRD) is commonly used for the characterization of materials, particularly the crystal structure and lattice parameter evaluations. It includes single-crystal and powder XRDs. The X-rays diffraction pattern essentially results from the combination of two different phenomenon (i) scattering of X-rays by each individual atoms lying in a plane and (ii) subsequent interference between the waves scattered by these atoms. This leads to the well known Bragg's diffraction. Well defined sharp peaks are obtained for crystalline lattice but the amorphous systems give broad hallows at low angles. It is well known that a crystalline lattice gives diffraction maxima at well defined 'θ' values (characteristics of the material) corresponding to different 'd' values for specified planes governed by Bragg's law

$$2d_{hkl} \; \sin\theta_B = n\lambda,$$

where, n is an integer, λ is the radiation wavelength, θ_B is the Bragg's diffraction angle and d_{hkl} is the distance between the reflecting parallel planes. The peak position (i.e. 2θ) is characteristic of the diffraction from a particular (hkl) plane (Azaroff 1968).

7.4.4   Fourier Transformed Infrared (FTIR) Spectroscopy

The FTIR spectroscopy is the technique used for the determination of molecular vibrational modes involving various structural bonds and groups in liquids, gases, powders, films, etc. In FTIR, determination of specific vibrational frequencies at which sample absorbs the IR radiation gives information about the functional groups or molecules present in the material, and hence information about the chemical specificity of the material. Any shift in these vibrational frequencies gives information about the possible interaction or changes occurring in the materials.

The FTIR spectrometer basically consists of a source of radiation in mid-infra-red region (viz., usually a silicon carbide rod known as globars), an interferometer

and a detector. The most commonly used detectors are made of pyroelectric deuterated triglycine sulphate (DTGS) and photo conducting mercury cadmium telluride (MCT). Interferometer allows simultaneous measurement of all the wavelengths in the MIR range and consists of a beam splitter, a fixed mirror, a movable mirror, and a drive and positioning mechanism. The intensity of the radiation at the detector is a function of the optical path difference of the beams in both the arms of the interferometer. Interferogram is obtained as a plot of intensity vs. wavenumber (cm^{-1}) using mathematical Fourier transformation (Kellner et al. 2004; Griffiths and Haseth 2007; Harris 2007).

7.4.5 Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR is a powerful technique used frequently to investigate the director structures within the microscopic cavities (Drzaic 1995; Pasini et al. 2003). It is equally applicable to submicron size droplets where optical methods fail to generate useful information due to higher wavelength of light as compared with the droplet diameter. Chemical specificity (Golemme et al. 1988b) and other aspects of nematic dispersion, including molecular orientation, rotation, diffusion, dynamic processes, interfacial effects in proximity to polymer surfaces, etc., have been explored using this technique. Both ^{13}C NMR and ^{2}H NMR have been used to investigate the PDLC films but usually the solid-state ^{2}H NMR is preferred over the ^{13}C NMR. In ^{2}H NMR, advantage is taken of the fact that deuteron possesses nuclear spin $= 1$ and a nonzero quadrupolar moment. There is an additional perturbative contribution in the energy level of deuteron coming from quadrupolar interaction between deuteron and the electric field gradient of the C–D bonds of the molecules. In the isotropic states, the perturbative contributions are completely averaged out in a single narrow line of width below 100 Hz by the molecular motion, but the same is not true for nematic(or other anisotropic) phase. In later case, single narrow line splits into a doublet with splitting being typically of the order of ~100 kHz. Since NMR spectrum reflects the response of all the molecules in a sample, its use for PDLCs system provides specific information about the contributions made by individual droplets (by their director configurations) in the spectra.

In PDLC films, both experimental and theoretical NMR spectra have been studied frequently to determine the director fields, orientations and diffusion within (or in between) the cavities (Crawford et al. 1991b; Buchert et al. 1993a, b). These studies include the detailed models of organizational and diffusional effects on the line shapes and splitting. Radial and bipolar orientations have been distinguished by diffusion properties of the nematic within the droplets (Golemme et al. 1988a). For radial droplets, molecular orientation is a sensitive function of position so diffusion changes the orientation of the molecule. In this case, NMR spectra observed earlier in the absence of (or slow) diffusion limit collapses into a single line centered at zero quadrupolar splitting in the presence of (or fast) fast diffusion limits. However, in bipolar droplet, nematic is oriented more-or-less in the same direction and

molecular diffusion makes only a partial averaging of the two lines of quadrupolar splitting in spectrum (Pasini et al. 2003). Further studies include, director alignment in the LC/polymer network system (Stannarius et al. 1991), electric field driven reorientation of submicron droplets (Aloe et al. 1991), weakly oriented ordered surface layer in the isotropic phase of a liquid crystalline material (Dolinsek et al. 1991; Crawford et al. 1991a, 1992).

Solid-state ^{13}C NMR technique has been used to understand the importance of the molecular motion of the liquid crystalline materials in switching phenomenon for PDLCs. A proper understanding of the switching behavior of LC molecules within the PDLC films will enhance its use by minimizing both the LC concentration and switching voltage while maintaining the good scattering properties of the PDLC films. Vilfan et al. (2003) have used low frequency proton NMR relaxometry in the kilohertz frequency range to study the spin–lattice relaxation of 5CB above nematic to isotropic transition in microdroplets of a PDLC film. Change in the mobility of the molecular segments of 5CB molecules in epoxy based polymer results due to increased interaction between LC and polymer. Molecular motion of LC within the droplet gets restricted due to decreased droplet size in PDLC films as a result of increased contact between the polymer matrix and the liquid crystal (Vilfan et al. 2003).

Apart from the afore-mentioned techniques some other approaches have also been used to determine the liquid crystal organizations in PDLCs. Angle-dependent light scattering studies (Zumer and Doane 1986; Zumer 1988; Whitehead et al. 1993) have been used to deduce the predominant liquid crystal configuration in PDLCs. Fourier transformed Raman spectroscopy has been used to provide chemically specific orientational information of the PDLC materials (Andreev et al. 1997). The order and dynamics of the LC material inside the nanosized droplets of a holographic PDLC film is recently investigated using ESR spin probe (Bacchiocchi et al. 2009). It determines the LC local director configuration inside the alternatively arranged LC nanodroplet and polymer layers.

7.4.6   Dielectric Relaxation Spectroscopy (DRS)

Dielectric relaxation spectroscopy is a well established technique to study the dynamics and motional behavior of liquid crystals in bulk as well as in confined geometries (Kramer and Schoenhals 2003; Kao 2004; Rzoska and Zhelezny 2004; Barsoukov and Macdonald 2005; Raikher and Shliomis 1994). When a dielectric material is placed in an external electric field E, dipole moment is induced in the material and it gets polarized under the influence of the field. One or more than one contributions, i.e., electronic, ionic, orientational and translational polarization may cause polarization in a dielectric material. Macroscopic polarization 'P' i.e., the average value of induced dipole moment per unit volume of the material is defined as the sum of the microscopic dipole moment $\mathbf{p_i}$ of individual molecules within the volume V,

$$\mathbf{P} = \frac{1}{V}\sum_{i} \mathbf{p_i} \tag{7.9}$$

In linear approximation, macroscopic polarization of a dielectric material is proportional to the strength of the applied external electric field $\mathbf{E}$:

$$\mathbf{P} = \varepsilon_0\, \chi \mathbf{E} \tag{7.10}$$

where, χ is the dielectric susceptibility of the material and $\varepsilon_0\,(=8.854 \times 10^{-12}\,\mathrm{F\,m^{-1}})$ is the dielectric permittivity of the free space.

According to Maxwell, matter can be treated as a continuum and the field inside the matter is the direct result of the electric displacement (electric induction) vector $\mathbf{D}$, which is electric field correction for the polarization:

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} \tag{7.11}$$

From (7.10) and (7.11), we get,

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \varepsilon_0\chi\mathbf{E} = \varepsilon_0\mathbf{E}(1 + \chi) = \varepsilon_0\varepsilon^*\mathbf{E} \tag{7.12}$$

where $\varepsilon^* = (1 + \chi)$ is called the relative permittivity or complex dielectric constant of the material. Normally ε^* is a complex quantity and is given by

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{7.13}$$

where, $j = \sqrt{-1}$, and, ε' and ε'' are the real and imaginary parts of complex dielectric constant (ε^*), respectively. In general, the real part of dielectric constant (ε') provides information about the charge storage capacity of the material, whereas imaginary part (ε'', also termed as dielectric loss) provides information about the loss from the material. Further, the ratio $\varepsilon''/\varepsilon'$ is used to obtain information about the dielectric relaxation processes occurring in the material and is described as loss tangent (i.e., tan δ)

$$\tan\,\delta = \frac{\varepsilon''}{\varepsilon'} \tag{7.14}$$

The relaxation processes occurring in the material are investigated by studying tan δ as a function of frequency of the applied signal and temperature. Either of the plots, i.e., tan δ or dielectric loss (ε'') vs. frequency of the applied signal gives a peak value, described by the relation $\omega\tau = 1$, where τ is the relaxation time and ω is the angular frequency of the applied signal (Kramer and Schoenhals 2003).

In PDLCs, dielectric relaxation spectroscopy has been used frequently to study the various interesting results related with anchoring effect and motion of the LC molecules in microscopic cavities (Jadzyn et al. 1999; Ganesan et al. 2009),

alignment and director order parameter of LC molecules (Williams et al. 2001), interfacial polarization process due to accumulation of charges at LC/polymer interface (Boussoualem et al. 2004), electro-wetting and reconfiguration effects (Fan et al. 2009; Ren et al. 2009), etc.

7.5 Droplet Morphologies and Director Configurations in PDLC Films

The confinement of LCs in microscopic droplets, their shape, size and alignment play a significant role in governing the ordering, dynamics, scattering and other electro-optical properties of PDLCs. These properties depend strongly upon the nature and composition of LC and polymer constituents, their refractive indices, solubility parameter, miscibility behavior, etc. Several groups are engaged actively in studying and characterizing the properties of PDLCs by using various binary and multi-component mixtures with other additives (Busbee et al. 2009; Pavani et al. 2009; Hinjosa and Sharma 2010; Cupelli et al. 2011; Zhou et al. 2011). In the following subsection, we provide a brief glimpse of some significant contributions made in this direction.

7.5.1 Droplet Morphologies

Polarizing optical microscopy has been used widely to perform morphological investigations on PDLCs. It shows the significant changes in the phase behavior of LCs confined in microscopic sized cavities as compared with their bulk counter parts. Various types of liquid crystal organizations such as axial, radial, bipolar, toroidal, etc. have been observed in PDLC films when observed through POM.

One of the earlier most studied PDLC film was prepared by using an LC mixture (E7) and side-chain liquid crystal epoxy polymers (LCEP) with cyanobiphenyl pendants (Chien et al. 1992). After the thermal induced phase separation (TIPS) process the POM images show radial nematic configurations which were quite different from the characteristic nematic textures observed earlier in pure LCEPs (Fig. 7.3a, b). Progress continues with the use of different LC and polymer materials to investigate the morphological changes observed in PDLCs when LC gets confined in microscopic cavities of polymers. For unpolymerized and UV-polymerized 2-ethyl hexyl acrylate (EHA) mixtures with E7, nematic droplets with a twisted radial structure inside the droplet have been observed (Roussel et al. 2000). It indicates the homeotropic anchoring at the polymer LC interface. As an effect of coalescence/diffusion phenomena significant changes in the size, shape, spatial distribution, number density, etc., of nematic droplets have been observed with the lapse of time (Fig. 7.3c, d). In the blends of polystyrene and EBBA (at different
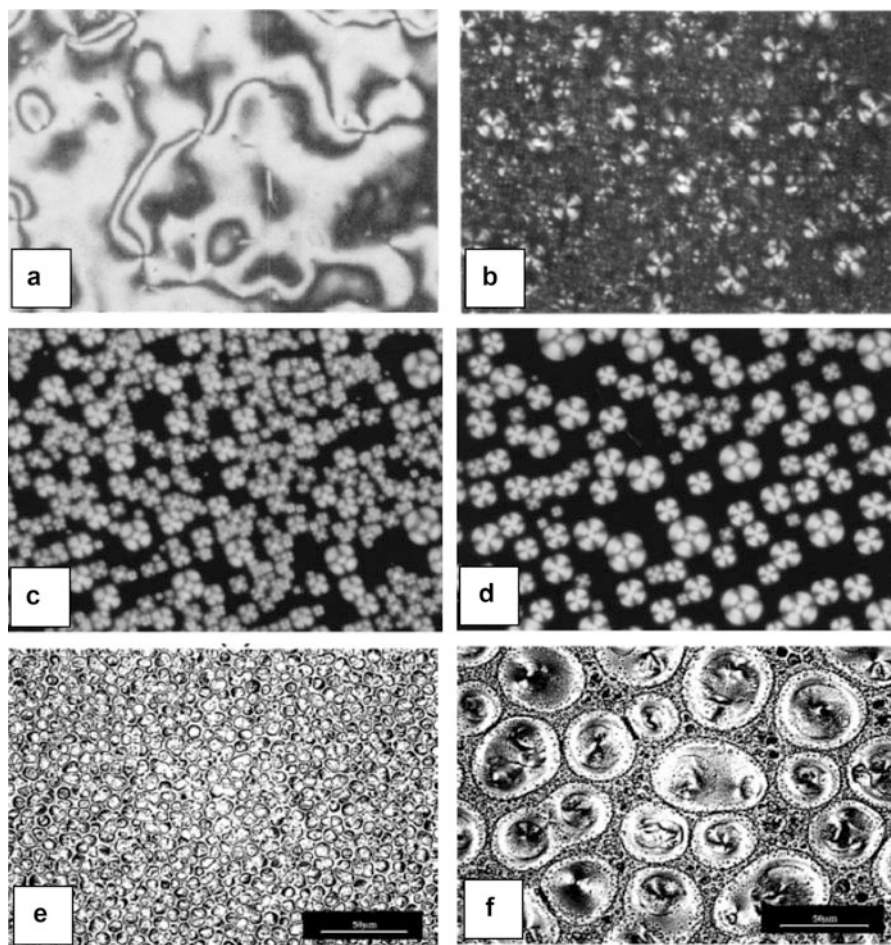
Fig. 7.3 POM images of (**a**) anisotropic LCEP-3 and (**b**) LCEP-3 dispersed liquid crystals (E7) (50/50) (Reprinted with permission from Macromolecules, 1992, **25**, 133–137. ©1992, American Chemical Society, Chien et al. 1992, Figure 2 and 3), PEHA/E7 (50:50) film as a function of time elapsed after UV exposure for (**c**) 30 min and (**d**) 15 h (Reprinted with permission from Phys. Rev. E., 2000, **62**, 2310–2316. ©2000, American Physical Society, Roussel et al. 2000, Figure 8), EBBA/PS (80:20) arising by (**e**) fast and (**f**) slow cooling from 130 °C (Reprinted with permission from Macromol. Chem. Phys., 2003, **204**, 928–935. ©2003, WILEY-VCH Verlag GmbH & Co KGaA, Weinheim, Hoppe et al. 2003, Figure 3d and 4d)

compositions), cooling at faster and slower rates results in the LC droplets of smaller and larger sizes, respectively (Fig. 7.3e, f). Changes in the phase diagram and different morphologies generated in these blends were studied by Hoppe et al. (2003).

Several other studies reveal that with changes in the surface anchoring conditions at LC/polymer interface, alignment of LC droplets gets changed. Polystyrene macro-iniferter (MI) has been used to control the alignment of LC molecules at the
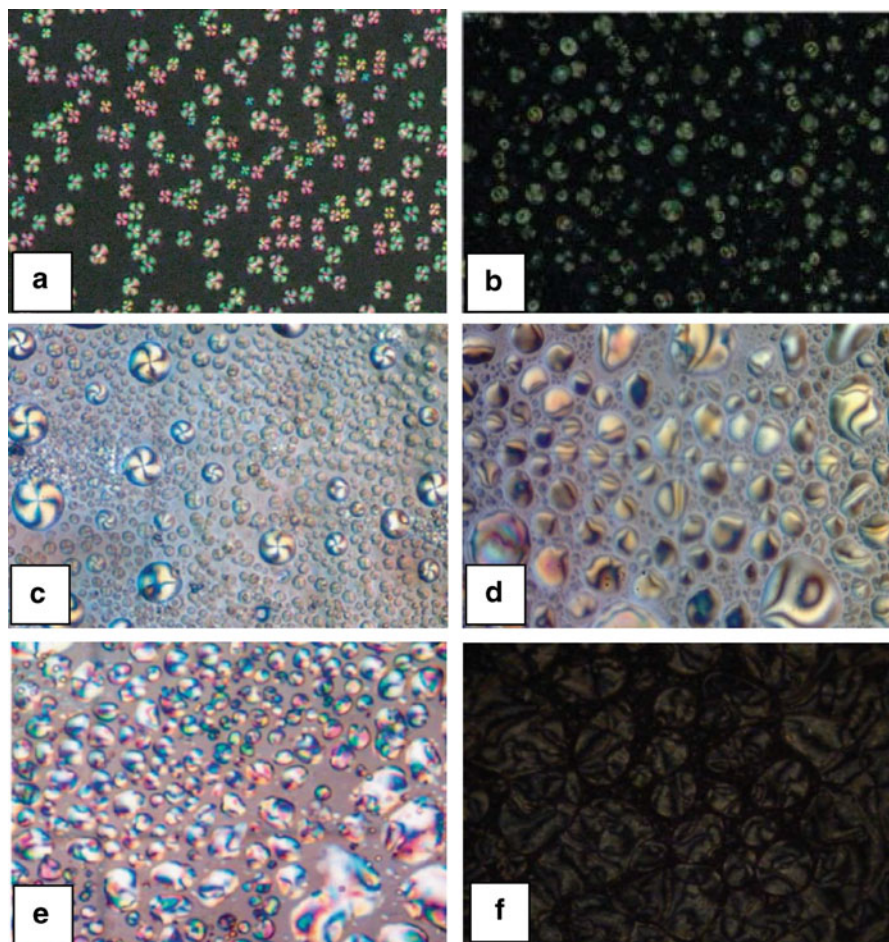
Fig. 7.4 POM images of PDLC films for MI:BA:E7 = 5:35:50 (by weight) using MI concentrations (**a**) 0.1 % and (**b**) 1 % (Reprinted with permission from Liq. Cryst., 2009, **36**, 933–938. ©2009, Taylor & Francis, Yan et al. 2009, Figure 4b and d), for 30 wt% and 75 wt% of UDBA in PMMA showing (**c**) radial and (**d**) bipolar configurations, for 75 wt% of DDBA in PMMA showing (**e**) randomly oriented nematic droplets (Reprinted with permission from Liq. Cryst., 2011, **38**, 849–859. ©2011, Taylor & Francis, Srivastava et al. 2011, Figure 4d and Figure 7c, d) and (**f**) for 60 wt% of UDBA in P(VdF–HFP) showing nematic droplets with schlieren textures (Reprinted with permission from Liq. Cryst., 2012, **39**, 1402–1413. ©2012, Taylor & Francis, Srivastava et al. 2012, Figure 4e)

droplet walls in PDLC films of butyl acrylate and E7 (Yan et al. 2009). Initially, at lower composition of MI, relatively small surface interaction favors the radial configuration which changes to bipolar one with increase in the composition of MI (Fig. 7.4a, b). Morphological changes observed in LC material consisting of decyloxy benzoic acid with different alkyl chains in PMMA matrix show that the randomly oriented nematic droplets and schlieren textures which were observed in

the pure mesogens get changed into radial (with maltese type crosses) and bipolar configurations. Change in the droplet morphologies due to the change in the polymer constituents and rate of cooling from an isotropic state have also been reported (Fig. 7.4c–f) (Srivastava et al. 2011, 2012).

Different types of morphological and electro-optical studies in PDLCs have been carried out as an effect of polymer viscosity, dye concentration, etc. Change in the droplet morphology and optical properties of PDLC films of a commercially available UV curable polymer NOA-65 and low molar mass nematic liquid crystal E-8 (BDH, UK) as an effect of temperature and applied voltage are shown in Fig. 7.5a, b. The POM images show LC droplets which have initially the bipolar configurations with random distribution of molecular axes get arranged into maltese type crosses with molecular axes oriented along the direction of applied electric field with increase in the applied voltage. Moreover, with increase in the temperature, effective voltage drops across the LC droplets. Consequently, the optical transmission and threshold voltage V_{th} decrease (Malik and Raina 2004). Effect of the polymer viscosity on the morphology of the PDLC films using ferroelectric liquid crystal ZLI-3654 and commercially available UV curable Norland polymers (NOA series of different viscosities) show that for unaligned films, LC droplet size increases with increase in the polymer viscosity whereas in aligned films, LC droplets get elongated along the rubbing direction of the alignment (Fig. 7.5c, d).

Also, dispersed films show that as compared with pure FLC, spontaneous polarization of the films decreases up to 50 % with increase in the polymer viscosity (Malik et al. 2003). Further, low viscosity based PDFLC film shows fast switching behavior than higher viscosity based PDFLC films (Malik et al. 2010). Optical contrast and electro optical response of the PDLC films may be tuned by using different concentrations of dyes as dopants in LC materials. Use of dye influences LC droplet size, and samples with low concentration of dye, provide an improved contrast ratio and reduced threshold voltage. The morphological changes observed as an effect of different concentration anthraquinone dye and applied voltages in PDLC films of NOA65 and E7 are shown in Fig. 7.5e–h (Kumar and Raina 2007).
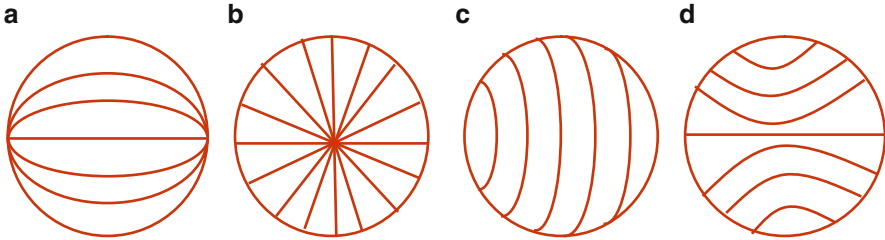
7.5.2   Director Configurations

Morphological investigations of various PDLC films show a number of LC configurations and their *inter-se* transformation within/in-between the droplets of a PDLC film. Usually, four common types of LC configurations which are *bipolar, radial, toroidal and axial* have been observed in these droplets (Fig. 7.6).

These configurations depend strongly on the size, shape and strength of interfacial interaction at LC/polymer interface and can be manipulated by external parameters, like temperature, electric field, magnetic field, etc. With variation in these parameters droplets in one configuration may become unstable and transformed into a more stable configuration. Basically two approaches are
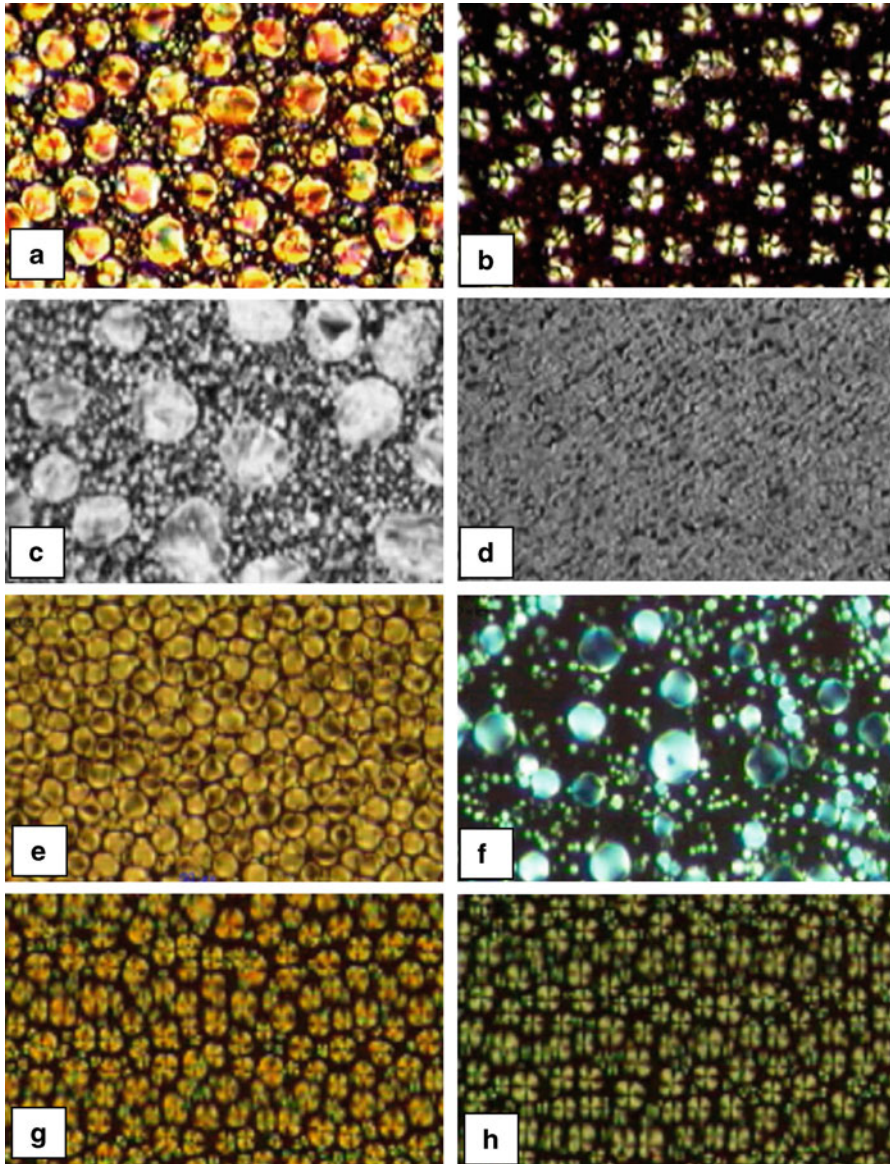
Fig. 7.5 Morphologies for PDNLC film at 55 °C in external field (f = 1 kHz) of (**a**) 5 V and (**b**) 25 V (Reprinted with permission from Optical Materials, 2004, **27**, 613–617. ©2004, Elsevier B. V., Malik and Raina 2004, Figure 1b, d), for PDFLC films using multi-component FLC mixture ZLI-3654 and UV curable polymer NOA-65 under (**c**) unaligned and (**d**) aligned conditions (Reprinted with permission from Current Applied Physics, 2003, **3**, 325–329. ©2003, Elsevier B. V., Malik et al. 2003, Figure 1c and Figure 3b),for DPDLC films with dye concentrations (**e**) 0.25 % and (**f**) 0.5 %, and, with applied voltages (**g**) 10 V and (**h**) 20 V on films with dye concentration of 0.25 % (Reprinted with permission from Curr. App. Phys., 2007, **7**, 636–642. ©2003, Elsevier Science B. V., Kumar and Raina 2007, Figure 3b, c and Figure 5c, d)

Fig. 7.6 Nematic director configurations: (**a**) bipolar, (**b**) radial, (**c**) toroidal, (**d**) axial

employed to analyze these droplet configurations. First one is based on analytical/ numerical approach and other one is on the computer simulation approaches. In specific situations, computer simulation gives a better result but approximations lead to a better understanding of the related phenomenon. In both the cases, numerical computation must also be performed. In analytical/numerical approach, droplet configurations have been discussed using certain basic assumptions (Zumer and Doane 1986; Bloisi and Vicari 2003):

1. Droplets are ellipsoidal (or more preferably spherical) in shape with a well defined droplet direction along the major axis under zero (or no external) field. These droplet directions get changed with the application of external field in such a manner that the droplet director ($\hat{n}$) be defined as the average direction of the nematic director inside the droplet.
2. Another assumption is the elastic constants approximations according to which
   $K_{11} = K_{22} = K_{33} = K$
   $K_T = K_{22}/K_{11}$; $K_B = K_{33}/K_{11}$; $K_T = K_B = K$

Bipolar and radial configurations result at zero fields with strong planner and homeotropic surface anchoring, whereas, toroidal and axial configurations are found for the conditions, $K_{33} \ll K_{11}$ and planer surface anchoring, and, $K_{33} \ll K_{11}$ and homeotropic surface anchoring, respectively. Some times more complex configurations like twisted configuration may also occur for larger values of splay elastic constant i.e., $K_{11} \gg K_{22} + 0.431\ K_{33}$ (Drzaic 1995).

7.5.3 Transformation Between the Droplet Structures

Within the LC droplets, transformations between different configurations provide information about the various physical parameters useful to describe the liquid crystalline states and also to explore their properties in device applications. Nematic droplets and their transformation between different configurations have been nicely discussed in literature (Drzaic 1995; Pairam and Nieves 2009; Kleman and Lavrentovich 2006; Leon et al. 2011a, b). Here we summarize, in brief, some basic transformation between these configurations.

Radial-axial configuration can be induced in a number of ways such as with the change in electric or magnetic field (Candau et al. 1973), surface anchoring energy, elastic constants, etc. Strong polar anchoring favors the radial structure whereas a strong external field induces axial structure. Axial structure can also be generated in the absence of external field if anchoring strength is sufficiently weak (Erdmann et al. 1990). A more detailed theoretical discussion for these transformations has been given by Zumer and Kralj (1992). Their results predict that the stability of radial-axial configuration depends on the relative value of the surface elastic constant i.e., K_{24} as compared with other nematic elastic constant. Calculations predict that K_{24} has only a minor effect on the director configuration within the radial or axial droplet but a more significant effect on the relative stability between these configurations. For sufficiently large droplets (1–50 µm) linear dependence on electric field and droplet size was observed for radial-axial transformation (Kovalchuk et al. 1988) but for very small droplets weak anchoring becomes more pronounced and favors the axial configuration.

The transformation between the *bipolar-radial and radial-bipolar* structure arises due to change in the surface alignment from parallel to perpendicular (Volvoik and Lavrentovich 1983). Starting with a bipolar droplet, transformation begins with a disclination (in the form of annular ring) on the droplet equator. With increase in the tilt angle as a change in the alignment, ring disclination moves towards the pole while point defect (boojums) at the pole becomes larger and dissipates. Once the ring defect contracts to a point defect it forms a point defect (hedgehog) which detaches from the surface and moves into the centre of the droplet forming a radial structure. Radial-bipolar transformation begins with the boojums at the pole and hedgehog moving towards the pole when alignment changes from perpendicular to parallel. Further, the intermediate states of the bipolar-radial and radial-bipolar structures are similar but not identical. Therefore, these transitions are not symmetric in the sense of possessing identical intermediate droplet configurations.

Besides the afore-mentioned droplet configurations within the droplets some other transitions have also been reported. These transitions are bipolar-twisted bipolar and bipolar-concentric (Drzaic 1988a), bipolar with twist wall (Reamey et al. 1992), radial-escaped radial (Xu et al. 1992) transition, etc. Additionally, cholesteric droplets also show several transitions such as, radial line (spherulite)—planer transitions (Yang and Crooker 1991; Kitzerow and Crooker 1992), helical unwinding of spherulite (Kitzerow and Crooker 1993), twisted helical transitions (Kurik and Lavrentovich 1982), etc. Defects play an important role in studying the various configurations within the droplet. They arise due to manipulation of the external parameters. Various configurations occur as a result of contraction between the line and point defects, associated escaped defects structures, and difference in the direction of rotation of nematic director on opposite sides of the droplet.

7.5.4 *Interfacial Effects*

In PDLCs films, different LC configurations occur due to change in interfacial properties at the LC/polymer interfaces. A number of constraints like, LC/polymer composition, their constituent, curing or exposure time to radiation, nature and concentration of the dopant, heating and cooling rates, etc., affect the interfacial properties in a typical PDLC film. Interfacial forces play an important role in determining liquid crystal anchoring (i.e., homogeneous or homeotropic) at the LC/polymer interface and also the droplet configuration (Erdmann et al. 1990; Mcfarland et al. 1993; Mirau and Srinivasarao 1997). Any small alteration in these forces may cause significant changes in LC droplet configuration. For large droplets of few microns size these changes can easily be observed using POM technique, but for very fine microscopic droplet other probes like NMR, IR imaging, AFM are used. Usually, solid-state ^{1}H and ^{13}C NMR are used to study the static and dynamic properties of interfacial regions in inhomogeneous materials (Crawford et al. 1991b, 1992; Allender et al. 1991; Cross and Fung 1992, 1993; Mirau and Srinivasarao 1997).

^{2}H NMR spectroscopy and relaxometry is a very sensitive technique to study the surface-induced order and molecular dynamics in isotropic phase of LCs in confined geometries. Due to the absence of the long-range orientational order in isotropic phase it is very useful in studying the surface interactions. It is also suitable for measuring the degree of orientational order in the isotropic phase for cylindrical, spherical and other irregular cavities. Vilfan et al. (1999a, b) have studied the two representative systems of confined LC (i) 8CB in cylindrical cavities of anopore membranes and (ii) 5CB with an embedded polymer network. They found substantial increase in the spin–lattice relaxation (T_1^{-1}) and transverse relaxation (T_2^{-1}) rates being stimulated by the surface induced orders. Measurement of T_1^{-1} provides insight into the molecular dynamics in confined LCs. In bulk isotropic phase, T_1^{-1} is increased due to local molecular reorientations which have at least one correlation time in nanosecond range. But in nematic phase, abrupt decrease in T_1^{-1} is observed, as the orientational ordering takes place and imposes limitation on the molecular rotational mobility. At temperatures much above the nematic-isotropic transition due to random motion of molecules both T_1^{-1} and T_2^{-1} are equal. But, for decreasing temperature near nematic-isotropic transition, T_2^{-1} attains a greater value due to short range anisotropy within the isotropic phase. Increase in T_2^{-1} provides information about the effect of spatial constraints on molecular mobility and on the surface orientational order parameter.

^{13}C-NMR provides a convenient method for the determination of order parameters of bulk LC by measuring the anisotropic chemical shift (Guo and Fung 1991, 1992). But it is also useful in investigating the orientational order of LC droplets confined in a polymer matrix. Roussel et al. (2002) have determined the orientational ordering of 5CB droplets confined in a polyethylhexylacrylate (PEHA) matrix using NMR and other probes. Aliphatic region of the spectra shows that the 2-ethyl hexyl fragment of the polymer chain is partially ordered due to

interdigitation with 5CB molecules at the polymer/LC interface. Moreover, due to higher chemical shift in anisotropic state, aromatic NMR signals were used for the calculation of the order parameter. Further, as suggested in the literature (Buchert et al. 1993a, b; Vilfan et al. 1995, 1999a, b), in smaller droplets enhanced LC/polymer contact limits the mobility of LC in the droplets as compared to LC in bulk. Its morphological study shows homeotropic anchoring of nematic director in droplets. It suggests that the polymer surface influences the surface orientational order and may lead to an increase of the nematic order in smaller cavities. It suggests that the interfacial effects at LC/polymer interface significantly affect the director orientational order of the nematic LCs in smaller cavities. Application of electric and magnetic fields might also increase the order parameter for confined LCs and also induce a transformation of the director configuration leading to radial or axial configuration (Crawford and Doane 1992; Erdmann et al. 1990). The aliphatic chains of the polymers are also known to provoke a surface induced order (Proust et al. 1972; Crawford et al. 1996; Amundson and Srinivasarao 1998; Roussel et al. 2000).

In other methods, AFM technique has been used for characterizing and understanding the interfacial effect in various PDLC films (Herod and Duran 1998a, b). Optical contrast mechanism (using IR imaging) has also been explored for getting specific information about interfacial effects as a change in refractive index near LC/polymer interface (Bhargava et al. 1998).

7.6 Electro-Optical Properties

There are a number of parameters which influence the properties of a PDLC film in device development applications. These are concerned with its film thickness, droplet size and shape, morphology, polymer plasticisation, composition, refractive indices, etc. Optimum voltage required to activate a PDLC device depends strongly on the thickness of the film. Both the average droplet size and its distribution play an important role in defining the microstructures for device applications. Scattering and reorientation properties of the film depend strongly upon the droplet size. A number of features of PDLC make it useful in various device development applications: (i) It does not require any rigid boundary and can be used to develop large and flexible films, (ii) It does not require any polarizer or other optical element except transparent electrode to provide optical contrast, thus useful in the development of compact devices and (iii) It requires much smaller amount of liquid crystal as compared with LC based devices, thus has an economic incentive also.

In generalized terms, basic principal of PDLC films operation includes field-dependent light scattering from the 'standard' nematic droplets. In these materials, scattering phenomenon depends on the refractive indices of LC and polymer constituents and also on the applied electric field, being 'typical' for most of the PDLCs. The other optical properties which have been explored in PDLCs are dichoric absorbance, reflection of polarized light, nonlinear optical effects, etc.

Depending upon the applied electric field (or voltage) other useful electro-optical properties include operating voltages and voltage holding ratio, optical contrast, PDLCs response time and switching speeds, memory effects, conductivity, polarization and depolarization effect, etc., in PDLC films (Vaz and Montgomery 1989; Zhang et al. 1992; Jain et al. 1993; Im et al. 1995; Drzaic 1995; Bouteiller and Barny 1996). The field-dependent properties of PDLC films are determined by both reactive and resistive effects (Drzaic 1995). Reactive effects are those which are out of phase with the applied voltage and stores energy within the film, while resistive effects are in phase and dissipate energy through the creation of heat. Depolarization charges and director reorientation in PDLC films appear as reactive elements, while movement of ions through the polymer and liquid crystal and other electrochemical processes at the electrodes are all examples of dissipative resistive elements. PDLC films are often discussed by an equivalent electric circuit model, in which film components are treated as a network of resistor and capacitor. In the simplest case, PDLC film consists of three elements, a parallel resistor and capacitor for liquid crystal/polymer composite and a series resistor for the conducting substance.

A brief description about some of the important electro-optical properties of PDLC films are given in the following subsections.

7.6.1 *Light Scattering Properties*

In PDLC due to mismatching between the ordinary and extraordinary components of the refractive indices of the LC materials and with the refractive index of the polymer matrix, light passing through the film gets scattered significantly. However, if there is no mismatch between the refractive index, light scattering vanishes. The amount of scattering depends upon a number of parameters concerning the state of polarization, angle of incidence, wavelength etc. of the incident light beam, various operating conditions like temperature, nature (waveform) and amplitude of the applied electric or magnetic fields, constituents, composition, dielectric, elastic and refractive index properties of LC and polymers, shape, size and distribution of LC droplets in PDLC films, etc. (Bloisi and Vicari 2003).

Initially, application of a suitable electric field aligns the LC molecules in a direction parallel to the field. As a consequence light incident normal to the field gets transmitted perfectly. But when the field is removed, due to change in LC orientation, incident light gets scattered randomly resulting a decrease in the overall transmittance value. The fundamental question in the light scattering problem is to determine the electromagnetic field at an arbitrary point in the surrounding medium of the scattering object (an LC molecule with certain dipole distribution in the case of PDLCs). Generally, superposition of electromagnetic fields coming from the incident light and the scattered one is taken into consideration for studying the scattering problems. Rigorous solution to the scattering problems are little tedious and beyond the scope of the present chapter. It involves certain assumption/

approximation related to anomalous diffraction, optical resonance, Raman scattering, Rayleigh scattering, Rayleigh–Jeans approximation, etc. and is described properly in literature (Van De Hulst 1957; Zumer 1988; Basile et al. 1993; Bloisi et al. 1995; Bloisi and Vicari 2003; Dick and Loiko 2001).

7.6.2 Response Time of PDLCs

PDLC films are often characterized by their ability to respond quickly to the changes occurring in the applied field, i.e., the rise and decay times. The time needed for transmitted intensity to reach (or fall) at 90 % of the saturation value, after application (or removal) of driving voltages are defined as 'rise' and 'decay' times, respectively. The typical orders of magnitudes of response time ranges from 1 to 10 ms for rise and 10 to 100 ms for decay times (Vaz and Montgomery 1989; Zhang et al. 1992; Jain et al. 1993). Dual frequency LCs mixtures have been used to speed up decay time. For applied field of low frequencies, it behaves as a positive LC and for high frequencies it behaves as a negative LC. PDLC film can be switch on by a low-frequency electric field, while a high frequency electric field is used to rotate LC molecules away from aligned direction. Some times cholesteric dopants are also used to reduce the decay time (Lu and Yang 1994).

7.6.3 Conductivity and Dielectric Properties of PDLCs

The inhomogeneous nature of the PDLC films along with intrinsic anisotropy of liquid crystals makes it interesting for various electric applications (Cupelli et al. 2009, 2011; Drzaic 1995). Since, both the conductivity and dielectric properties of the liquid crystals are anisotropic, depolarization fields across the droplets depend upon its (droplet) orientation. The movement of ions and the creation of depolarization field affect both the reorientation and dynamics of LC droplets inside the PDLC films. Therefore, change in the LC droplet size and director orientations can be explained by making use of polarization and depolarization fields. Polarization charge opposes the local field so it can either reduce or enhance the local field in different portions of the film. With application of an external field, movement of ions establishes a depolarization field in the direction opposite to the applied field. As a result, effective field across the LC droplets reduces (a Maxwell–Wagner effect) in the whole PDLC film (Rout and Jain 1992a, b; Zhong et al. 1992; Kuriakose et al. 2014). If the polymer is more conductive than the LC material, polarization field will enhance the field across the LC droplets. A reduced (or enhanced) field across the droplet requires a higher (or lower) external voltage applied to the films for droplet reorientation.

Ionic motions in the film can be frozen out if the frequency of the applied signal is high enough. It also becomes insignificant if the ionic concentration within the

film is very low. It can be explained by considering that in PDLC films, polymer matrix serves the role of a trapping medium for the motion of ions, so there would not be sufficient number of ions to create significant depolarization field. Another possibility is associated with orientation of droplets that exerts an alignment effect on the neighboring droplets (Drzaic 1995; Cupelli et al. 2009, 2011). The dipolar fields, i.e., the mean dielectric constant of the medium, surrounding these droplets depend on the extent of orientation of neighboring droplets. As long as the dielectric constant of the polymer and liquid crystal differ, bound depolarization charges will enhance the field across one medium at the expense of the field across the other. As a result, even in the limit of zero-conductivity field across the droplet will not be equal to the applied field. Since, PDLC film represents a mixed dielectric, change in its free energy density with applied field results due to contributions both from the liquid crystal and polymer components. Initially, the free energy density of the liquid crystal portion in PDLC film changes due to reorientation of LC molecules with the application of the field. This reorientation of LC molecules also alters the depolarization field across the polymer and causes a change in the free energy density of the polymer portion of the film. As LC gets more and more aligned, it increases its dielectric constant and depolarization field across the polymer portions of the film. Consequently, the total field and the free energy density across the polymer portion of the film decreases.

The conductivity of the polymer and LC components influence the operation of PDLC in various ways, i.e., fringing field effect, shielding effects, electrode effects, image stacking (Lowe and Kriss 2006), etc. Mobile ions within the film move under the influence of external field, setting up a depolarization field which tends to cancel the applied field. The nature of the depolarization field depends on the relative conductivity of the polymer and liquid crystals. If the LC is more conductive than the polymer, charge will be build up at the LC/polymer interface which tends to cancel the field across the droplet. Increasing the conductivity of the polymer allows the charge to leak into the polymer, thereby reducing this depolarization effect. However, if the film becomes too conductive, charges accumulate at the electrode interfaces and cancel the field across the entire film except near the electrodes. Moreover, conductivity is relative and depends on the frequency of the applied field (or voltage). If the time scale of interest is slow enough to allow the ionic moments to influence the field across the film, it becomes more conductive, but for sufficiently high frequencies film conductivity invariably gets suppressed.

7.6.4 Reverse Mode Operation in PDLCs

Contrary to the normal PDLCs, reverse mode PDLCs have high OFF state transparence which turn opaque in ON state. Actually, the anchoring characteristics of LCs at the polymer/LC boundaries play the key role in determining the ON and OFF states transmittance. For reverse mode PDLCs, in OFF state, the built-in DC electric field aligns uniformly the LC director orientation and leads to a high

OFF state transmittance. However, in ON state due to depolarization of built-in DC electric field (either from bound or mobile charges) the LC director orientation gets distributed randomly and an opaque ON state is observed. Built-in DC electric field is developed due to separation of ionic impurities at LC droplet/polymer interface when a high intensity electric field (i.e., a charge process) is applied to the PDLC film for some time. Such phenomenon is also known as Maxwell-Wagner effect (Rout and Jain 1992a, b; Zhong et al. 1992). It depends strongly on the charging temperature, charging field and charging time. Higher values of these parameters result in the higher value of built-in DC electric field. To avoid the ion remix, field is usually stored during the cooling process. Modulation in the built-in DC electric field allows transmittance tuning in PDLC films with change in its morphological, dielectric and surface anchoring properties (Rout and Jain 1992a, b; Zhong et al. 1992). It also converts the conventional quadratic electro-optical response of PDLC into a quasi-linear one (Blinov et al. 1998; Nicoletta et al. 2000)

Reverse mode PDLCs are preferred in various building and automotive applications (Hikmet 1990, 1992). Reverse mode PDLC films with positive dielectric anisotropic liquid crystal E49, polymer polymethylmethacrylate (PMMA) and lipophilic ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) as dopant have been prepared and studied by Cupelli et al. (2011). They found that the use of ionic liquid as dopant setups a large built-in DC electric field in PDLCs and give OFF state transmittances up to 75 % with uniform alignment to LC director configuration. In another work, they have studied self-adjusting smart windows based on reverse mode operation PDLC (Cupelli et al. 2009). Photoconductive material (zinc phthalocyanine) and ionic liquid (1-hexyl-3-methylimidazoliumbis (trifluoromethylsulfonyl)imide) were used as dopant. This self-adjusting chromogenic material is suitable for external glazing and is also able to self-increase its scattering as a function of the impinging light intensity.

7.6.5 Non-linear Effects in PDLCs

Nonlinearity has an important role in the development of PDLCs and some very interesting non linear effects have been observed in PDLCs. These include studies related with second harmonic generation (SHG), laser irradiation, Brags diffraction, Kerr effect, quasi linear response, etc.

In PDLCs, LC/polymer interface acts as a non centro-symmetric object and produce *SHG* when irradiated with light beam of sufficient intensity. Initially, when there is no phase separation, i.e., in isotropic polymer/nematic state, SHG signals were not observed. But, with increase in anisotropy, surface structures are defined more clearly and SHG signal occurs significantly. SHG signals are also affected with the application of field due to typical index matching of the dielectric constant of the LC and polymer when nematic gets oriented properly (Huang and Chen 1991; Yuan et al. 1991).

Several nonlinear optical effects based on the *laser heating* of PDLC films have been investigated (Simoni et al. 1989, 1990, 1991, 1992b; Cipparrone et al. 1990). Using a four-wave mixing process self-transparency effect in PDLC films have been studied. Initially, spatially varying refractive index grating was formed due to local heating of the material. Local heating occurs in the high intensity areas of the interference pattern when two lasers of the same frequency cross at small angle. Further, grating diffracts the two incident waves to create two new waves, and thereby completing four-wave mixing process. Until the laser intensity has reached a threshold value no diffraction pattern was observed but above the threshold, additional diffracted beams were observed (Simoni et al. 1992a). The response time of these effects was of the order of tens of milliseconds, consisted with thermal effects as the source of the behavior. For increasing the absorbance of the laser beam sometimes dyes have also been used (Simoni et al. 1989; Cipparrone et al. 1990). In another work laser beam of lower intensities and AC field below threshold have also been used (Simoni et al. 1992b).

Interfering laser beams have been used to set up a permanent *diffraction grating* profile in photopolhymerized PDLC films (Lackner et al. 1989; Sutherland 1989; Sutherland et al. 1993, 1994; Tanaka et al. 1993, 1994). Sutherland has differentiated between Raman–Nath and Bragg-type gratings developed in these films (Lackner et al. 1989; Sutherland 1989; Muhoray and West 1989). Macroscopically, Raman–Nath gratings show multiple diffraction orders while microscopically it shows a gradual variation in droplet size or density. For Bragg gratings, a single diffraction order is observed macroscopically while microscopically the film shows sharp boundaries between areas containing a high droplet density and the areas with virtually no droplets.

Sansone et al. (1990, 1994) have observed *Kerr effects* in PLDC films using submicron droplet sizes. In Kerr effect, fluid exhibits the properties of uniaxial crystal due to induced birefringence when electric field is applied. At molecular level, Kerr effect for an isotropic state arises due to contributions from molecular hyper polarizability, anisotropic polarizability and permanent dipole moments of the constituent molecules. However, for liquid crystals it depends on the collective molecular rotation of the constituent molecules. In the liquid crystals, reorientation of the molecular director also changes the refractive index which leads to larger value Kerr constants as compared with isotropic fluids. This effect has been used to minimize the scattering form PDLC films of submicron sized droplets, thereby increasing the transparency of the films (Sansone et al. 1990, 1994).

7.7 Time Dependent Phenomenon in PDLCs

Several studies reveal that the phase, morphology, reorientation dynamics, LC/polymer composition, etc., in PDLCs are influenced significantly with the evolution of time (Drzaic 1988b; Challa et al. 1995). Various interesting results

occur when PDLC films are monitored at different time scales during the process of curing and electrical treatments. Change in the morphology, and electro-optical properties of PDLC films have been reported with change in the curing time (i.e., time of exposure to UV or other radiations). Field induced reorientation processes are found to be quite complex for different time scales in microsecond to millisecond range (Drzaic 1988b).

7.7.1 Time Evolution of PDLC Films

The phase separation processes in PDLCs have been studied extensively by a number of groups (Mcfarland et al. 1993; Challa et al. 1997a, b; Wall and Koenig 1998; Bhargava et al. 1999). They have investigated the evolution of the droplets using visual and IR spectroscopic methods. In one of the works, Mcfarland et al. (1993) have found that with evolution of time, the IR bands associated with the polymer gets broadened while the bands associated with the LC became narrower. They attributed that with phase separation polymer becomes less fluid (and leads to broadening of associated IR bands) while LC becomes more fluid (and leads to narrowing of associated IR bands). It suggests that in the typical PDLC there is a continuous occurring of phase separation process with evolution of time. In their later works, they reported studies related with diffusion liquid crystal in polymer regions by IR micro spectroscopic imaging (Challa et al. 1997a, b; Wall and Koenig 1998). For better understanding of the phase separation process light scattering (Golemme et al. 1998), IR methods (Wall and Koenig 1997; Bhargava et al. 1999) have been used along with other techniques (Roussel et al. 1998).

7.7.2 Dynamics of PDLC Films

Dynamic light scattering (Mertelj et al. 1997; Mertelj and Copic 1998) and theoretical (Kelly and Muhoray 1997) studies on PDLC droplets show significant difference in the properties of the droplets as compared with bulk LC materials. These differences lead to a change in reorientation dynamics of PDLCs and result mainly due to confinement of LC into microscopic polymer cavities, interfacial interactions at the LC/polymer interface and contributions from elastic constant terms to the free energy (Zumer and Doane 1986; Kitzerow 1994) in a PDLC film, with change in the shape, size, interfacial interaction, LC configuration, etc.; dynamics varies for both between the droplets and with the droplets (Drzaic 1988b; Wu et al. 1989; Lin et al. 1995; Brazeau et al. 1998).

7.8 Theoretical Developments in PDLCs

Dispersions of liquid crystal molecules in flexible polymer matrices are interesting as the multi-component systems that furnish valuable information on the coupling between the two species (Drzaic 1995; Klosowicz and Zmija 1995; Serbutoviez et al. 1996; Simoni 1997). They combine the common properties of polymers and liquid crystals. Most of these PDLCs exhibit liquid–liquid immiscibility which leads to the formation of mesogenic phases during cooling cycle. Interesting changes in the isotropic-nematic phase transitions have been observed with variations in the compositions of the constituents. Mesogenic changes observed in PDLCs can be studied by their thermal and morphological investigations and construction of the equilibrium phase diagram. Flory–Huggins (FH) theory (Flory 1953) for the isotropic phase of mixing, Maier–Saupe (MS) theory (Maier and Saupe 1959, 1960) of nematic orders and its generalization by McMillan to include smectic ordering (McMillan 1971) have been used widely to understand the effect of polymers and LC constituents on the equilibrium phase diagram (Shen and Kyu 1995; Chiu and Kyu 1995; Riccardi et al. 1998a, b; Benmouna et al. 1998, 2000; Roussel et al. 2000; Soule et al. 2009).

The properties of PDLCs are quite sensitive to both the polymer and LC constituents in the mixture. Large differences have been observed due to change in one of these two constituents (Riccardi et al. 1998a, b; Benmouna et al. 1999; Hoppe et al. 2003; Mucha 2003). Polystyrene (PS) with commercially available nematics like 8CB, E7 and EBBA has been widely used to investigate the phase diagram and concept of miscibility in PDLCs (Riccardi et al. 1998a, b; Benmouna et al. 1999,2000; Roussel et al. 2000; Hoppe et al. 2003; Soule et al. 2009). Miscibility of polymers has attracted much attention because it provides a route to improve compatibility between different polymers and other immiscible counterparts (Lejardi et al. 2011).

Poly(ethylene oxide) (PEO) is one of these miscible polymers, utilized in the formation of a triblock copolymer having some LC content (Zhou et al. 2011). It is a semi-crystalline material with spherulite structure having lower melting point and two glass transition temperatures T_G (Jin et al. 2002; Zhou et al. 2011). With the addition of some kind of diluents, appreciable changes in the microstructures and phase diagram of PEO have been observed (Talibuddin et al. 1996; Srivastava et al. 2012). Poly(methyl methacrylate) (PMMA) is also a useful polymer in studies related with PDLCs (Chen and Shanks 2007; Deshmukh and Malik 2008; Ganesan et al. 2009; Zhou et al. 2011). It exhibits useful electro-optical and mechanical properties and offers higher thermal stability to the PDLC films. Another important class of polymers consists of vinylidene fluoride (VdF). Because of its fluorine constituent, it is easily cross-linkable to form a homopolymer of VdF itself, i.e., PVdF or other copolymers, having different fluoroolefins like tetrafluoroethylene, hexafluoropropylene, etc. (Tatemoto et al. 1981; Ameduri 2009). The PVdF based polymers support partial crystallinity with microporous geometry having high thermal and mechanical stability. These polymers have shown their importance in

various studies related with the polymer gel electrolytes as well (Abbrent et al. 2001; Huang and Wunder 2001; Cheng et al. 2004, 2005; Xi et al. 2005; Kim et al. 2009; Vijaykumar et al. 2009; Shirey and Maranas 2009; Wu et al. 2010; Zalewska et al. 2010). Dielectric relaxation spectroscopic investigations have been carried out to study the hindered motion of LC in PVdF based polymer cavities (Ganesan et al. 2009).

Some other common polymers used in the PDLC applications are: epoxy based polymers (Smith and Vaz 1988), ethyl hexyl acrylate (EHA) (Im et al. 1995; Roussel et al. 2000; 2002), ethoxy benzylidene butylaniline (EBBA) (Hoppe et al. 2003), NOA series polymers (Zhou et al. 2004; Kumar and Raina 2007), PN314 (Williams et al. 2001), PlatSil Gel (Zou and Fang 2011), PolyBed (Russell et al. 1995), Polybutyl methacrylate (PBMA) (Manohar et al. 2006), Polysilixane (Bedjaoui et al. 2004), etc.

The general equation:

In PDLCs, the thermodynamic phase behavior of polymers and LC materials are usually described by combining the theoretical methods developed separately for LCs and polymers (McMillan 1971; Shen and Kyu 1995; Chiu and Kyu 1995, 1998; Riccardi et al. 1998a, b; Mucha 2003). The analysis of the experimental data provides useful information about the effects of the polymer size, transition temperature and interaction mechanism on the isotropic to nematic (and/or smectic) transition (Benmouna et al. 1998, 1999, 2000; Roussel et al. 2000, 2002; Hoppe et al. 2003; Boussoualem et al. 2004; Soule et al. 2009). The total free energy of a system is written as a sum of two contributions (i) the free energy, $f^{(i)}$ for isotropic state of mixing described by Flory–Huggins lattice model and (ii) the anisotropic contribution to the free energy, $f^{(a)}$ due to the occurrence of mesoscopic transitions.

$$f = f^{(i)} + f^{(a)}. \tag{7.14}$$

The choice of the two contributions depends on the nature of transitions for the phases in equilibrium. The equilibrium may exist either between two isotropic phases or one isotropic and one anisotropic (nematic/smectic) phase or one isotropic and two anisotropic (both nematic and smectic) phases. The free energies for these phases have been explained by a combination of FH theory of isotropic mixing, the MS theory of nematic order and McMillan model to include smectic order. A brief description of these theories follows:

7.8.1 Flory–Huggins Theory

In this model (Flory 1953; Orwoll and Arnold 1996; Schuld and Wolf 1999; Krevelen and Nijenhuis 2009) the free energy density of a binary mixture under mean field approximation is expressed as

$$\frac{f^{(i)}}{k_B T} = \frac{\varphi_1}{N_1}\ln\varphi_1 + \frac{\varphi_2}{N_2}\ln\varphi_2 + \chi\varphi_1\varphi_2 \tag{7.15}$$

where φ_1, φ_2 and χ represent, respectively, the volume fraction of liquid crystal, polymer material and FH interaction parameter. N_1 and N_2 are the number of molecules of liquid crystal and polymer, respectively. Parameter χ is often used to obtain the best fit with the experimental data in the portion of the phase diagram where the isotropic interactions are most significant. It is defined by the relation

$$\chi = A + \frac{B}{T} \tag{7.16}$$

Here, A and B are constants independent of temperature.

7.8.2 Mair–Saupe–Macmillan Theory

In the Maier–Saupe theory, it is assumed that the polymer chains are flexible having no mesogenic part and the anisotropic contribution to the free energy is only due to the nematic ordering (Maier and Saupe 1959, 1960; De Gennes 1974; De Gennes and Prost 1993, 1995; Chandrasekhar 1977; Singh 2000, 2002). McMillan (1971) generalized this theory to account smectic ordering as well (Chandrasekhar 1977; Singh 2000, 2002). Thus in PDLCs the relative contribution of anisotropic free energy to the total free energy is strongly dependent on the order parameters. The nematic and smectic order parameters S and σ are described, respectively, by the relations,

$$S = \langle P_2(\cos\theta_{12})\rangle \tag{7.17}$$

and

$$\sigma = \frac{1}{2}\left\langle (3\cos^2\theta - 1)\cos\frac{2\pi z}{d}\right\rangle \tag{7.18}$$

where, P_2 is the second rank Legendre polynomial, θ_{12} is the angle between two molecular axes, θ is the angle between the director of LC molecules and reference axis and d is the inter layer spacing between consecutive smectic layers. The angular bracket denotes the ensemble averaging.

Using McMillan's idea for smectic ordering, the partition function for generalized Maier–Saupe–McMillan theory includes terms for both the nematic and smectic ordering and is given by the relation

$$Z = \iint d\cos\theta \, dz \, \exp\left[\frac{m_n}{2}(3\cos^2\theta - 1)\right]\exp\left[\frac{m_S}{2}(3\cos^2\theta - 1)\cos 2\pi\frac{z}{d}\right] \tag{7.19}$$

where, m_n and m_S are the mean-field parameters which are described in terms of order parameters S and σ,

$$m_n = \nu S \varphi_1; \quad m_s = \zeta \nu \sigma \varphi_1 \tag{7.20}$$

Here $\nu = 4.54 \frac{T_{NI}}{T}$ represents the Maier–Saupe quadrupole interaction parameter and ζ is the strength of smectic interaction to incorporate the McMillan's idea in the MS theory. It depends on the ratio of T_{SN}/T_{NI}. With this generalization, the overall anisotropic contribution to the free energy is given by the relation,

$$\frac{f^{(a)}}{k_B T} = \frac{\varphi_1}{N_1} \left[-\ln Z + \frac{1}{2} \nu \varphi_1 \left(S^2 + \zeta \sigma^2 \right) \right] \tag{7.21}$$

Using the afore-mentioned theories, miscibility and phase behavior of LC/polymer constituents in PDLC films have been well studied and reported in the literature (Shen and Kyu 1995; Chiu and Kyu 1995; Riccardi et al. 1998a, b; Benmouna et al. 1999, 2000; Roussel et al. 2000; Hoppe et al. 2003; Soule et al. 2009; Lejardi et al. 2011; Srivastava et al. 2012).

7.9 Applications of PDLCs

Due to their peculiar electro-optical and mechanical properties PDLCs have been used in various device development applications and are beneficial over LCs based devices. For example, some of the important PDLCs applications are—eye protection viewer (Land and Schmitt 1995), flexible displays (Sheraw et al. 2002), holographic PDLCs (Sutherland 1991; Sutherland et al. 1994, 1998), heat-resistant PDLC light modulator (Takizawa et al. 1999; Fujikake et al. 2000), spatial light modulator (Vicari 2003), projection displays (Shikama et al. 1995; Kikuchi et al. 2000), dichoric dye based displays (Bahadur 1991; Drzaic et al. 1990, 1992; Drzaic 1991), direct view scattering mode and cholesteric displays (Nolan et al. 1993; Fujikake et al. 1993), scattering polarizers (Aphonin 1995, 1996; Bloisi et al. 1996, 1997), sensors (Parmar and Singh 1992; Tabib et al. 2000; Jain and Thakur 1992; Jain et al. 1993), smart windows (Lampert 1998; Sanchez et al. 2002; Drzaic and Muller 1989), second harmonic generators (Li et al. 1991; Macdonald et al. 1998), etc. These applications have been nicely described in literatures (Bloisi and Vicari 2003; Drzaic 1995).

7.10 Recent Advances in PDLCs

In spite of a large number of meticulous reports on polymer dispersed liquid crystals (PDLCs) during the last three decades, it is still a promising field of research and has the potential to divert the attention of workers for contributing in this area. Present section provides a brief account of the streamlined works

carried out in last few years in the area of PDLCs, liquid crystal droplets confined in other microscopic cavities, and interpenetrating liquid crystals and polymer networks.

Electro-optical investigations of PDLC films have been a part of considerable research for several research groups. Alteration in any of the polymer, LC and other constituents or operating conditions effect significantly the electro-optical properties of the PDLC films (Kashima et al. 2010; Dzhons et al. 2011; Song et al. 2012a, b; Liu et al. 2012a, 2013; Shao et al. 2012, 2014; Lu et al. 2013; Yang et al. 2014). Doping has a significant contribution in modifying the electro-optical and other intrinsic anisotropic properties of PDLCs. Multidirectional light-controlled reflective PDLC film with doping of dye has been reported with enhanced contrast ratio and image brightness of the films (Jeon et al. 2012). PDLCs with reverse mode operations have been studied in polymerized mixtures of liquid crystalline monomer (1,4-bis{4-(6-(acryloyloxy)hexyloxy)benzoyloxy} benzene and the eutectic nematic liquid crystal (ZLI 4788, Merck chemicals) doping with single walled carbon nanotubes (Filpo et al. 2012). Reverse mode PDLCs using cetyltrimethylammonium bromide (CTAB) coated on ITO glass have also been prepared by the vertical alignment of LCs (Lee et al. 2014). In both the studies significant changes in the electro-optical properties of the PDLC films have been reported due to presence of doped materials.

In some other works, NMR relaxometry studies in low frequency regions (of few MHz) show significant increase in the proton spin–lattice relaxation rates in the nematic and smectic phases of 8OCB LC molecules embedded in nano-porous airosil matrix (Rajeswari et al. 2012). In this work authors have also reported that the individual dynamic processes like translational diffusion and reorientation of the molecules within the voids remain unaffected due to confinement. Liu et al. (2012b) have characterized the optically switchable photonic crystals based on SiO_2 inverse opals infiltrated with photoresponsive liquid crystal, viz., a mixture of nematic LC (E7) and photochromic LC, 4-butyl-4-methyoxyazobenzene (BMAB). They reported that nematic-isotropic phase transition of E7 inside the opals is triggered by the trans-cis isomerization of BMAB upon UV photoirradiation and leads to a change in refractive index contrast between E7 and SiO_2 inverse opal (Liu et al. 2012b). Drastic changes in the electro-optical properties of the PDLC films consisting of photosensitive monomer (NOA65) and nematic liquid crystals (E7) have been reported by using montmorillonite (MMT) clay as dopant after being modified by conducting pentamerous oligoaniline (POA) (Tsai et al. 2012). The transmission contrast ratio of the films was found to increase by five times whereas the driving voltage is lowered by almost 70 %. Significant decrease in the PDLC response time has also been obtained.

Another tool which has been explored widely in the field of PDLCs is related with its holographic techniques. It has been studied so intensively that a separate abbreviation HPDLCs is given to these types of PDLCs. Dramatic changes in the electro-optical properties of PDLCs and various device fabrications have been reported using HPDLC. Interest is still a burgeoning area to work (Zheng et al. 2012; Diao et al. 2014; Jang and Kim 2011; Liu et al. 2012c). Some of the

recently developed applications of HPDLC includes rewritable holograms based on azobenzene containing liquid crystalline polymers (Shishido 2010), liquid crystal lasers as a ultrathin and highly versatile laser sources having wideband tenability, large coherence and multidirectional emission capability (Coles and Morris 2010), dual wavelength distributed feedback laser empowered by dye-doped HPDLC (Diao et al. 2012), linear variable optical filters using a single beam one-step holographic interferometry method (Moein et al. 2014), monochromatic visible light photointibtor for storage of colored 3D images (Peng et al. 2014), HPDLC based photonic quasicrystals for linearly polarized low threshold lasing (Luo et al. 2012), etc.

Confinement of liquid crystal in microscopic cavities results in a number of complicated director fields which depends on the size and shape of the drop, presence of external field, elastic properties of LC, anchoring and other topological constraints on the LC director at the boundaries of the drop, i.e. the confining volume (Leon and Nieves 2011). Recently, very interesting studies on the morphogenesis of the defects and disclination in liquid crystals confined in different geometries during phase transitions (Leon et al. 2011a, b; Kim et al. 2013), controlled generation of the defect lines by imposing topological constraints on nematic microdrops in handledbody-shaped silica structures (Campbell et al. 2014), effect of colloidal dispersion on the topology of liquid crystals for self-assembling of composite material with pre-engineered properties and structures in different non-trivial configurations like, a superstructure of knot-shaped particles linked by nematic field (Martinez et al. 2014), control over the number and orientation of defects by functionalizing the unavoidable defects with the help of spherical colloid particles, coated on the thin layered nematic liquid crystal shell of varying thickness (Leon et al. 2011b), design of functional soft materials based on the confinement induced LC ordering, triggered by interaction with bio-molecular species and self assembling of amphiphiles (Miller et al. 2014), generation of double armed helical patterns by using paramagnetic polystyrene particles actuated by weak magnetic field and its control by an out-of-plane electric field (Navarro et al. 2011), etc. have been reported. Laser directed self assembled and facile erasable defect clusters and control of optical phase singularities in liquid crystals with probable applications in data storage, singular optics and other electro-optic devices have also been reported (Ackerman et al. 2012).

Self-assembled liquid crystals and LC polymer gels with interesting microstructures and electro-optical properties have been reported, recently, using photoinduced and some other techniques. Self-assembled randomly dispersed polymerized network of lysine based gelator and nematic LC molecules have been obtained by the formation of hydrogen bonds in the isotropic phase of the nematic LC molecule (Eimura et al. 2012). After the isotropic–nematic transition light-scattering nematic LC gels are formed which exhibits electro-optical switching between light scattering and transparent states with comparatively lower driving voltage than the non-polymerized LC gels. Philippe et al. (2011), have reported a 2D photoinduced self-organized periodic structure of commercial NLC mixture and photocurable reactive mesogens which gets stabilized in terms of morphology and electro-optic

response with application of strong electric field. Discontinuous volume change in a nematic liquid crystal cross-linked polymer gel containing small amount of azobenzene molecules and swollen by another nematic solvent (i.e., 5CB) has also been reported by Hayata et al. (2012). Volume change occurs near nematic-isotropic phase transition temperature of the LC polymer gel, due to loss of nematic order within the gel by trans-cis photoisomerization of azobenzene when exposed to UV irradiation. Magnetic-field directed self-assembly of a liquid crystalline block copolymer with brush-type architecture has been reported as a platform for creating functional materials (Deshmukh et al. 2014). Nematic LC-polymer network composite formed by photo-polymerization of the monomer under externally applied electric fields shows that the polymer network stabilizes both the director and electric polarization of the LC (Hicks et al. 2013).

Graphene oxide (GO) is a novel class of material exhibiting uniform electro-optical properties over an ultra-large GO sheet. Flow and filed induced birefringence in the phase sequence of GO has shown the occurrence of phase transitions from isotropic to biphasic and biphasic to nematic phases (Shen et al. 2014). These GO-LC response is very sensitive to external stimulus. Shen et al. (2014) have reported an extremely large Kerr coefficient that is about three orders of magnitudes greater than the commonly known values for molecular liquid crystals. Due to extremely large Kerr coefficient it finds application in fabricating electro-optic devices with macroscopic electrodes, as well as well-aligned, defect-free GO sheets over wide areas. For further processing and fabrication of more complex architectures using GO dispersion its rheological behaviour for isotropic to LC and LC gel phases have been studied using ultra-large GO sheets (Naficy et al. 2014). It has been demonstrated that GO dispersions exhibit unique viscoelastic behavior, whereas the rheological behavior varies considerably with dispersion concentration.

7.11 Future Perspective and Challenges

Liquid crystals are partially ordered systems without a rigid, long-range structure. They are intermediate in symmetry and structure between the solid crystalline state and amorphous isotropic liquid state. The advancement in the knowledge of its chemical structure, physical properties and technical applications coincided with a period of rapid expansion in terms of the physical techniques available to the materials. This, together with great advances in the theory of condensed matter and the rapid progress in computer simulation techniques made liquid crystals an exciting area for scientific research with many fundamental challenges. On the other hand, polymer is a large molecule composed of identical structural unit (monomers), typically bonded by a covalent chemical. The polymerisation reaction leading to formation of polymer from the monomer, often requires a short initiator that might be the addition of a chemical initiator or the exposition to high energy UV photons. Due to the existence of both resistance and flexibility, they show

interesting mechanical properties. A very important step in the historical development of mesogenic materials took place in 1984, when Fergason prepared a polymeric film embedded with very small droplets (0.1–100 μm) of mesogenic materials. These kinds of materials are called polymer dispersed liquid crystals (PDLCs). These composite materials are simply a mixture of polymer and liquid crystal. PDLCs, consisting of micron sized LC droplets dispersed in a polymer matrix, are promising electro-optic material for displays, storage devices, light switches, tunable focus lenses, privacy windows, reverse mode PDLCs, photointibitor and so forth. Depending on the nature, properties and concentration of the polymers and the liquid crystals, a large variety of structures are possible in PDLCs. The study of PDLCs has attracted considerable attention, in recent decades, from the points of view of basic understanding as well as industrial and technological applications. A multi-disciplinary approach has emerged to be the essential necessity of studies in PDLCs, and, those working in the area are expected to have familiarity with the chemical constitution of the materials and their properties, together with the knowledge of the physics of the phenomenon which they exhibit. In our understanding a better knowledge of the structure and properties of polymer dispersed liquid crystals is of fundamental significance because of the exotic nature of their properties and continued requirement of technological applications. In view of these, the subject matter discussed in this chapter is full of challenge and curiosity.

In brief, from the studies on PDLCs we can conclude that there are large number of variables like solubility parameter, solubility limit, fraction of liquid crystal in LC rich domains inside the polymer matrix, composition of mesogens, polymer constituent, etc., which influence the PDLC film formation. Various other parameters like temperature, rate of cooling, applied field strength, exposure time to radiation, constrained on the surface anchoring, etc., have also significant effect on the droplet morphologies and electro-optical properties of PDLC films. Tuning among these variables would be useful in getting the PDLC films with uniform dispersion over a larger area for specific applications.

This chapter concerns with various techniques which have been used frequently in the preparation and characterization of PDLC films. Several other factors are also important to determine how these materials would be useful in commercial and scientific developments. Some of the problems which need to be encountered in future are given below.

Effect of surface anchoring on droplet configurations, order parameters and morphologies of the mesogens due to their confinement in homogeneous materials needs to be explored using NMR, AFM, IR imaging and other techniques. A more elaborate work to study the scattering phenomenon in PDLCs is also desired. Proper theoretical explanation for the observed changes in LC director configuration in microscopic droplets and other complex geometries is still lacking. Computer simulations are to be the best hope to provide answers not only to these interesting and important questions but also to resolve many issues regarding the structure and properties of PDLC films. The future directions of work in this area are likely to be the computer simulation and more neat-clean experimental data.

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