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PHOTORESPONSIVE LIQUID CRYSTALS

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Photochemical transformations of molecules in liquid crystalline media can bring about changes in their phase transition characteristics or alignment. This ability to amplify molecular level processes into macroscopic phenomena arises due to the cooperative interactions and long-range ordering of liquid crystalline molecules. Various aspects regarding the design and study of such photoresponsive liquid crystals and their use in development of optical switches and imaging devices are discussed.

Key Words: Liquid Crystals; Photoisomerization; Optical Switching; Isothermal Phase Transitions; Photoalignment

1 Introduction

Interest in the study of photochemical and photophysical processes in organized assemblies has largely been driven by efforts to use the constrained matrices provided by such assemblies to control the excited state properties of guest molecules. For example, the rigid environment provided by some of the microassemblies can be utilized for carrying out photochemical reactions in a stereo-, regio- and enantiospecific manner[1-4]. Similarly, variations in viscosity, polarity and pH in constrained media can be used to control the excited state lifetimes and luminescence properties of guest molecules[4-7]. In tune with these studies, earlier reports on photochemical and photophysical processes in liquid crystalline (LC) media have also mainly concentrated on utilizing the anisotropic and constrained environment of LCs to control the excited state behaviour of guest molecules.[8-11] Most of these studies have been reviewed[8].

A far more interesting aspect of the study of photochemical processes in liquid crystalline media is where photochemical transformations can bring about modifications in the alignment or phase transition properties of the liquid crystalline host[12-14]. In these systems, weak photochemical processes occurring at the molecular level are translated into macroscopic phenomena due to the cooperative interactions and long-range ordering of liquid crystalline molecules, leading to amplification of the signals. Currently available display devices based on liquid crystals use electric field induced switching, which possess switching times in the order of several milliseconds. In photoresponsive liquid crystals, switching times can be several orders of magnitude higher making them potentially important in a number of advanced photonic applications such as memory storage, optical computing, high-speed communication and real-time holography.

2 Classification and Optical Properties

The structure and properties of liquid crystals have been extensively reviewed[15-24] and only a brief description is provided here. Liquid crystals form a class of condensed phase, where the molecules possess a degree of orientation, intermediate to that of highly ordered crystals and isotropic liquids. They form supramolecular assemblies with unidirectional orientation of their molecular axes to give rise to optical anisotropy. Liquid crystals can be broadly classified as lyotropic, where the mesomorphic phase formation is solvent induced and thermotropic, where the mesophase formation is thermally induced. This account mainly deals with the photoresponsive aspects of thermotropic LCs. Thermotropic LC phases are predominantly observed in organic compounds, which are rod, disc- or board-shaped. According to their microscopic organization, liquid crystalline phases are broadly grouped into four major classes namely nematics, cholesterics, smectics, and discotics

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(Fig.1). In the nematic mesophase, the molecules are aligned with their long axes parallel to each other. Cholesteric or chiral nematic phases are observed in optically active molecules or by nematic liquid crystals containing optically active dopants. In this phase the director (a unit vector signifying the average direction of the molecular long axis) of an individual layer is twisted through a small angle with respect to the director of the adjacent layer resulting in a helical arrangement of the layers. The thickness required for the director to turn through 360° represents the pitch length (p) of the helical arrangement in cholesterics. In a smectic mesophase, the molecules are not only aligned parallel but are also arranged in such a way that the centres of adjacent molecules lie in a plane. Smectic phases can be further differentiated depending upon the packing arrangement of the molecules within the layers and the angle of the directors to the layer plane. Discotic phases are generally exhibited by disc shaped molecules where these molecules can pack in a nematic-like arrangement or as vertically stacked columns.

The anisotropic packing of liquid crystals imparts unique optical properties to this class of materials[16,25,26]. Most mesophases exhibit birefringence whose intensity is dependent upon the difference of the refractive index parallel and perpendicular to the director, angle of incidence of light on the surface and wavelength of light. As a result, the polarization of light can be altered as it passes through the mesophase. Normally mesophases exist in a non-oriented fashion containing domains of differing alignment (Fig. 2), and these generally possess a milky and non-transparent appearance due to internal light scattering.

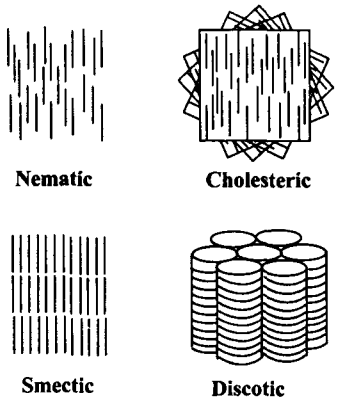


Fig. 1 Pictorial representations of the molecular shapes and orientations of the major liquid crystalline phase types

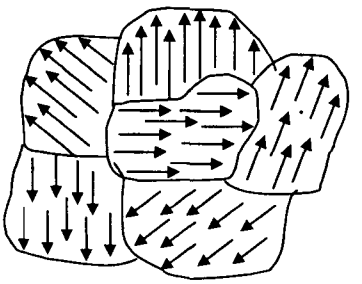


Fig. 2 Representation of several domains in a mesophase having different alignment.

Liquid crystals can be oriented macroscopically using mechanical, electric or magnetic forces, to form optically clear films[25]. A typical example of a macroscopically oriented liquid crystal cell is shown in Fig. 3a, where the top and bottom surfaces of the liquid crystal cell have been treated to align the molecules perpendicular to each other. The intervening layers arrange themselves in a twisted manner as shown in the figure, due to the influence of the neighbouring molecules. In such a cell, known as the twisted nematic cell that is used in conventional liquid crystal display devices, the plane of polarization of transmitted light will also be twisted by 90° as depicted in Fig. 3a[27]. The unique helical ordering of cholesteric liquid crystal molecules on the other hand induces selective reflection of the wavelengths satisfying the relationship, $\lambda = np$, where n is the refractive index of the liquid crystalline material and p is the helical pitch length (Fig. 3b)[28]. The ability to control these and other unique optical properties of liquid crystals by modifying their alignment and phase transition behaviour forms the principal basis for design of liquid crystal based optical switches.

3 Photoswitching in Liquid Crystals

Photophysical and photochemical processes in liquid crystals can bring about changes in the alignment or phase transition properties. Earlier

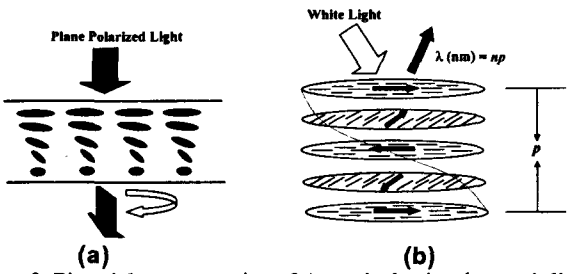


Fig. 3 Pictorial representation of a) a typical twisted nematic liquid crystal cell and b) helical ordering of layers in cholesteric liquid crystals.

studies utilized the heat content (thermal-mode switching) of light to bring about such changes. More recently, it has been shown that photochemical changes (photochemical-mode) can be utilized to bring about these transformations in a more selective manner.

3.1 Thermal-Mode Switching

In thermal-mode switching, regions of local overheating are created with a laser beam in homeotropically-aligned smectic, cholesteric or smectic/cholesteric mixtures between transparent indium tin oxide (ITO) coated glass plates[29,30]. In these local regions, the liquid crystalline phase changes to an isotropic melt thereby destroying the homeotropic alignment. On cooling, scattering polydomains are formed in this region (Fig. 4). Such laser addressed liquid crystal light valves can generate stable images with high spatial resolution and contrast ratio[31]. The image can be erased by applying an electrical field as depicted in Fig. 4 The long-term stability of images could be significantly improved by using polymeric LCs[32,33].

In the earlier devices optically transparent ITO electrodes were used to absorb the laser light and convert it into heat. The heat thus generated is conducted into the LC layer resulting in local isotropization, and the necessity for heat transfer from the glass substrate to the LC layer results in an increase in the write-in time. Also, the spread in heat energy results in the loss of resolution of images. Imaging by thermal-mode switching could be substantially improved by doping the LCs with a light absorbing dye such as Ni chelates, which are photochemically inert and nonfluorescent. The predominant pathway for loss of excitation energy in these Ni chelates is via radiationless (thermal) processes with lifetimes of 10^{-11} to 10^{-13} s. These complexes can rapidly "dump" heat uniformly into the LC medium. Further improvement in the resolution of the image in the "thermal-mode" switching could be obtained by doping the LCs with photochemically inert dyes possessing high dichroic ratios[34].

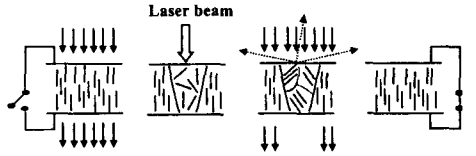


Fig. 4 Representation of thermal-mode imaging on oriented nematic LC film[34].

3.2 Photochemical Switching

In contrast to thermal-mode switching, photochemical switching is brought about by chemical transformations of either the guest molecules dissolved in LC matrices or of the LC molecules themselves. Both reversible and irreversible photochemical transformations can be utilized for switching applications. For example, photo-decomposition of cholesteryl iodide in LC mixtures comprising of cholesteryl iodide and cholesteryl nonanoate resulted in a change in their selective reflectivity[35]. Due to the irreversible nature of this photoreaction it is not possible to erase images stored in this manner. Phase transitions as well as alignment changes of LCs brought about by photochemical transformations which are thermally or photochemically reversible are of more interest since they can be used for the design of erasable-direct-read-after-write (EDRAW) systems[13,36-42].

4 Photoinduced Phase Transitions

4.1 Host-Guest Systems

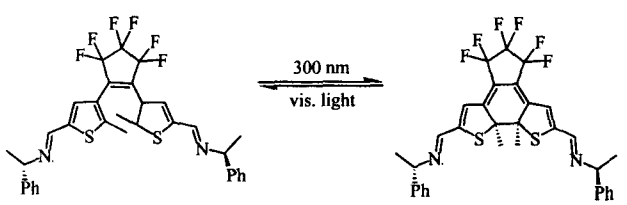
The presence of extraneous molecules can reduce the isotropization temperatures of LCs, and the extent of reduction can vary with the shape of the molecule. For example, when nematic or smectic LCs are doped with rod-shaped *trans*-isomers of azobenzenes the isotropization temperature of the host LCs are not significantly altered, whereas large depression in the isotropization temperatures can be observed when the bent *cis*-isomers of azobenzenes are used as dopants[12,41]. Thus photoisomerization of *trans*-azobenzenes dissolved in LC matrices held close to their isotropization temperatures can result in isotropization. Recovery of the LC phase becomes possible by reconversion of the *cis*-isomers of azobenzenes to their *trans*-form either thermally or photochemically. Since photochemically induced phase transitions do not involve a change in temperature, they are termed as isothermal phase transitions. Apart from azobenzenes, photochromic molecules such as spiropyrans, fulgides and stilbenes, which can undergo significant changes in their molecular shapes, can be used as dopants to bring about photoinduced iso-thermal phase transitions[43,44]. The various parameters that control photoinduced isothermal phase transitions in host-

guest systems, such as the nature of the host LCs, photochromic guest, concentration of the guest as well as temperature, have been extensively investigated[45-48]. Photochemical phase transitions in host-guest systems where the host is a liquid crystalline polymer has also been extensively investigated[49].

The dynamics of phase transition in LCs doped with azobenzenes has been examined by Ikeda and co-workers using time-resolved birefringence measurements[50]. Excitation by 355 nm pulsed laser resulted in photoisomerization of the azobenzene dopant which leads to the isotropization of the LC host. Loss of birefringence in the irradiated region resulted in reduction in the transmission of light through the crossed polarizers. The time required for total loss of transmittance, which corresponds to the time required for the isothermal phase transition was observed to be ~100 ms. Confirmation that the phase transition was indeed due to photochemical transitions and not due to 'thermal-mode' switching, was obtained by the absence of isotropization when a model azobenzene derivative, which does not undergo photoisomerization, was used as the dopant. The time required for nematic-isotropic switching was the same for LC polymers doped with azobenzene derivatives.

Photoswitching between nematic and cholesteric phases have been investigated using chiro-optical molecular switches. Nematic liquid crystals can be converted into cholesteric using chiral dopants[51]. By doping the nematic LC with just sufficient amount of chiral dopant needed for the formation of cholesteric phase only in one photostate, a reversible nematic to cholesteric photoswitching can be produced. For example, the photoisomerization of enantiomerically pure bisimine (Scheme 1) doped in a commericially available nematic LCs, such as ZL1-389 and K_{15} resulted in reversible switching between cholesteric and nematic phases[51].

Irradiation of the nematic LCs doped with the acrylic ester-substituted bicyclic ketones (Chart 1)



Scheme 1 Photoisomerization of enantiomerically pure bisimines[51].

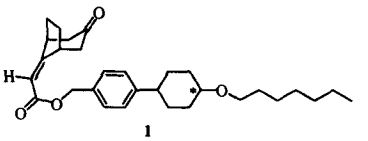


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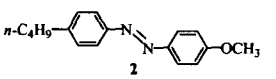
Chart 1

using circularly polarized light resulted in a nematic to cholesteric phase transition due to formation of enantiomeric excess of the dopant[52].

4.2 Intrinsically Photoactive Liquid Crystals

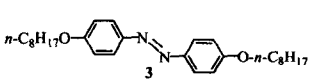
Photoisomerization of azobenzene derivatives is a very fast process and generally occurs in the picosecond time domain. The relatively long time required for photoinduced isothermal phase transitions in azobenzene doped LCs can be attributed to the time required for the host LC molecules to react to the formation of the *cis*-isomer of the azobenzene dopant. It would therefore be possible to reduce the response or switching times for photoinduced isothermal phase transitions by designing LC molecules, which are intrinsically photoactive.

The azobenzene chromophore is ideally suited for the design of intrinsically photoactive liquid crystals, since its *trans*-isomer stabilizes the LC phase whereas its *cis*-isomer destabilizes it. Ikeda and coworkers have developed monomeric and polymeric azobenzene derivatives (Chart 2) which are nematic in their *trans*-form and isotropic in their *cis*-form[41,53-55]. Photolysis of thin films (~200 nm) of the *trans*-isomer of the low molecular weight azobenzene derivatives leads to isotropization due to the formation of the *cis*-isomer. Time-resolved measurements of the changes in the birefringence indicated that the photoinduced isothermal phase transition occurred in about 200 μs, which is several orders of magnitude faster than the rate of



2

K 35°C N 48°C I



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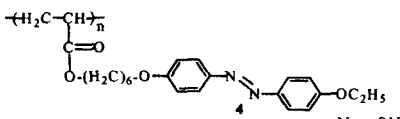
K 99°C N 113°C I



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G 45°C N 155°C I $Mn = 9100$ $Mw/Mn = 1.3$

Chart 2

photoswitching observed in host/guest systems. In these systems the thermal *cis-trans* isomerization is very fast (~30 s) and hence long-term storage of the image is not possible.

The polymeric LC (PLC), **4**(Chart 2) possess a much larger nematic temperature range. Irradiation of the PLC derivative also led to isothermal phase changes and the rate of change was similar to that reported for the low-molecular weight LCs. Interestingly, a nematic to isotropic phase transition with similar switching times could also be observed on irradiation of the PLC below its glass transition temperature (T_g)[41,55]. Although at room temperature the thermal *cis-trans* isomerization occurred within about 24 h the image formed remains stable for extended periods of over a year. The images could be erased however by heating the polymer film above its T_g. Based on the changes in the dichroic ratios of the azobenzene chromophore between the various states, the mechanism shown in Fig. 5 was proposed to explain the storage of information in the PLC below its T_g[41].

In the glassy state (below Tg) the azobenzene chromophores exist in an ordered state as in the nematic phase. Irradiation resulted in a *trans-cis* isomerization of the azobenzene chromophore, which leads to a loss in the dichroic ratio as shown schematically in Fig. 5. The dichroic ratio did not recover even after the thermal *cis-trans* isomerization was complete, indicating that the *trans-* isomers were reformed in a randomly aligned manner. The randomly aligned azobenzene chromophores could not reorient due to the rigidity of the PLC film below its T_g and thus forming a stable image.

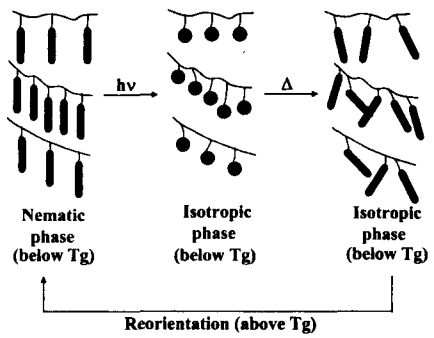


Fig. 5 Orientation of *trans*-azobenzene mesogens after the *trans-cis-trans* cycles. The orientation of the *trans*-azobenzene mesogens is random after the thermal *cis-trans* back isomerization and this random orientation is fixed below the Tg of the polymer. The nematic phase can be restored if the temperature is raised above Tg[41].

The optical switching behaviour of polymer azobenzene LCs has also been investigated using reflection-mode analysis. Optical switching observed in the reflection-mode could be repeated over ten thousand cycles, which was ten times more stable than that observed in the transmission-mode analysis. Although the response time in the switching was 100 μs, which was similar to that observed in the transmission-mode the recovery of the nematic phase occurred in 1 ms which was about six times faster[54].

LC materials can also be obtained through non-covalent interactions such as hydrogen bonding, ionic, charge-transfer and ion-dipolar interactions between complimentary structural elements. Photoswitchable LCs can be designed by selecting a photoresponsive chromophore as one of the elements. Kato *et al.* have reported on a hydrogen bonded liquid crystalline polymer complex between a polymeric hydrogen bond acceptor **5** (Chart 3) and 6-[(4-octylphenylazo) phenoxy] hexanoic acid (**6**)[56]. The hydrogen bonded complex between the acceptor and 6-[(4-octylphenylazo) phenoxy] hexanoic acid exhibited a nematic phase between 47-93 °C. Sequential UV and visible light irradiation caused reversible photo-chemically induced nematic-isotropic phase transitions.

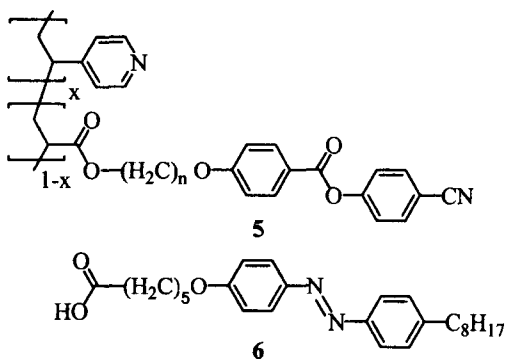
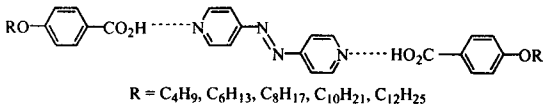


Chart 3

The liquid crystalline behaviour and photoswitching characteristics of LCs formed via hydrogen bonding between 4,4′-azobipyridine and 4-alkylbenzoic acids have been reported (Chart 4). On photolysis the supramolecular hydrogen bonded assemblies undergo a smectic to crystalline phase transition[57]. A number of other hydrogen bonded LCs containing substituted 4′-azopyridine as the hydrogen bond acceptor have been synthesized and investigated[58]. Photoinduced phase transitions were not observed in most of these systems and



R = C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$

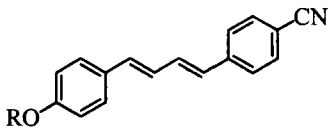
7

Chart 4

this could be attributed to substantial enhancement in thermal *cis-trans* isomerization of the chromophore on hydrogen bonding, which does not allow sufficient amounts of the *cis*-isomer to build up on irradiation.

With a few exceptions, most systems designed for photoinduced isothermal phase transitions have utilized the azobenzene chromophore. A drawback associated with azobenzene derivatives is that the *cis-trans* isomerization is thermally facile and additional measures, such as use of polymer LCs have to be used. Liquid crystalline materials derived from butadienes possessing thermally stable photoisomers have been synthesized (Chart 5)[59-61]. Whereas the *EE* isomers of these butadiene derivatives possess LC phases, their *EZ* and *ZE* isomers are non-liquid crystalline[61].

Photolysis by 360 nm light of thin LC films of these diphenylbutadienes held between quartz dics resulted in isothermal formation of isotropic phase. On photolysis with 360 nm, in the LC state, a steady state mixture rich in *EZ* and *ZE* isomers was obtained. Complete reversal of the *EZ* and *ZE* isomers to the *EE* form could be obtained by photolysis using light of a different wavelength, in the solid state. Under these conditions the photoisomerization becomes very stereospecific.



8, R = CH_3 **10**, R = C_8H_{17}
9, R = C_4H_9 **11**, R = $C_{12}H_{25}$

Chart 5

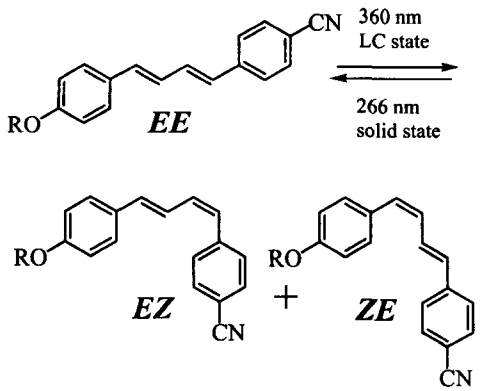
Table 1

Phase transition temperatures and thermodynamic parameters of the diphenylbutadiene derivatives (Chart 5)[61].

Compound	Phase transition temperatures (°C)[a]	DH(kJmol^{-1})	DS(JK^{-1}mol^{-1})
8	K 175.3 N 213 I	21.1 (K-N)	47.0 (K-N)
9	K 141.5 N 209.1 I	25.8, 0.4	85.1, 0.9
10	K 105.3 S 159.6 N 186.6 I	36.2, 0.4(N-I)	95.7, 0.9(N-I)
11	K 96.9 S 171.9 I	46.2, 3.4	124.7, 7.6

[a] K = crystalline, N = nematic, S = smectic A and I = isotropic

As reported for related chromophores the *EE* isomers do not undergo photoisomerization in the solid state, whereas the photoisomerization of the *EZ* and *ZE* remains feasible under these conditions[62-65]. Using this principle complete reversal between the LC and isotropic phases could be obtained over several cycles.



Scheme 2. Photoisomerization of alkoxy-cyano-substituted diphenylbutadiene liquid crystals (Chart 5)[61].

5 Photoinduced Alignment Changes in Liquid Crystals

Photochemically induced changes in alignment of LCs have been extensively investigated in recent years. Both in-plane and out-of-plane alignment of LCs can be achieved allowing two and three-dimensional storage of information. Various aspects regarding photoinduced alignment have been recently reviewed[12,13].

Reversibly isomerizable chromophores such as azobenzene are known to undergo reorientation when irradiated with plain polarized light in rigid polymeric media. The change in alignment can be easily discerned on measuring the angular dependence of absorbance of the chromophore at its absorption maximum using polarized light, which arises due to the dichroic nature of the molecule[66-70]. The dichroic ratio (R) of a molecule is given by,

$$R = A_o / A_\perp \qquad ...(1)$$

where, A_o and $A_\perp$ are the absorbance measured with the polarized beam parallel and perpendicular to the optical axis of the molecule. The dichroic ratio of azobenzene derivatives is fairly high[71,72]. A schematic representation of the change in angular dependence of absorption before and after irradiation of azobenzene in a polymeric film using plane-polarized light is given in Fig. 6.

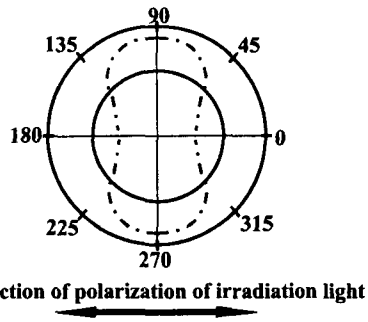


Fig. 6 Schematic representation of angular dependence of absorption of azobenzene in polymer film before (inner circle) and after irradiation (dotted curve).

Before irradiation the azobenzene chromophores are randomly aligned and the absorbance is the same in all directions as represented by the radius of the circle. Following irradiation, the intensity of absorption perpendicular to the plane of polarization of light increases whereas the absorption parallel to it decreases. This is caused by selective absorption of light by the azobenzene chromophore aligned parallel or closely parallel to the plane of polarization of the irradiation source and conversion of these molecules to their *cis*-form. Thermal isomerization of the *cis*-isomer will lead to randomly aligned *trans*-isomers, which due to the rigidity of the medium will be frozen into the new alignment until excited again. On prolonged irradiation, chromophores possessing their molecular axis aligned closely parallel to the plane of polarization will undergo repeated *trans-cis-trans* isomerization whereas those with their molecular axis aligned perpendicular would remain unaffected. This eventually results in most of the azobenzene molecules being perpendicularly aligned to the plane of polarization of light. Heating the polymers above their Tg can erase the induced alignment.

The ability of photoresponsive molecules like azobenzene to undergo reorientation on irradiation by polarized light can be utilized to bring about photoalignment of LCs[13,73]. This can be achieved either by doping the LCs with photoresponsive molecules or incorporation of such molecules on the surface of cells containing the LCs. The mechanism of photoalignment in LCs doped with a photosensitive molecule on irradiation is shown schematically in Fig. 7.

Irradiation of azobenzene doped LCs results in alignment of the axes of the azobenzene molecules perpendicular to the plane of polarization. Due to

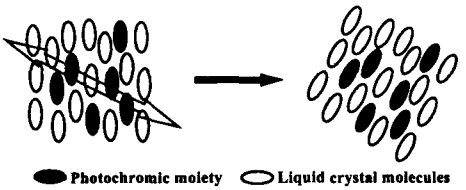


Fig. 7 Molecular reorientation of photochromic LCs irradiated with linearly polarized light resulting in a cooperative photoreorientation of LC molecules[13].

the cooperative interaction and long-range ordering of LCs the host LC molecules also align their axes parallel to that of the photochromic molecules. The photoinduced alignment is short-lived in low-molecular weight LCs. This is due to thermal randomization of the *trans*-isomers of azobenzene due to the fluid like environment provided by the low-molecular weight LCs. Stable alignment could be obtained by incorporating the azobenzene chromophores as pendants in cross-linked polymers[74]. The efficiency and stability of alignment is dependent on the nature of LC host, photochrome, temperature and intensity of light[75-79].

Undoped liquid crystals as well as liquid crystals doped with photochemically inert dyes are also known to undergo reorientation. Reorientation in such systems is proposed to arise from the local electric field induced by the irradiation source[80,81].

An interesting effect arises when polymeric films containing azobenzene chromophores are irradiated using unpolarized light. This results in the realignment of the azobenzene chromophores along the direction of propagation of light, since this is the only direction in which the azobenzene chromophore cannot absorb unpolarized light. Using this method three-dimensional control of alignment of photochromes becomes achievable. Further control in the three-dimensional alignment can be obtained by varying the incident direction of the irradiation light. This type of three-dimensional alignment, which has potential use in the development of high-density information storage devices, has been reported in a large number of PLCs[82].

Another interesting effect of *trans-cis* photoisomerization of azobenzene doped in smectic hosts is the reversible increase in the smectic A layer spacing[42,83,84]. Experimental and computer simulation studies suggest that the effect can be attributed to the photochemically formed *cis*-isomers being driven from within the smectic layers to locations between the layers as depicted in Fig. 8.

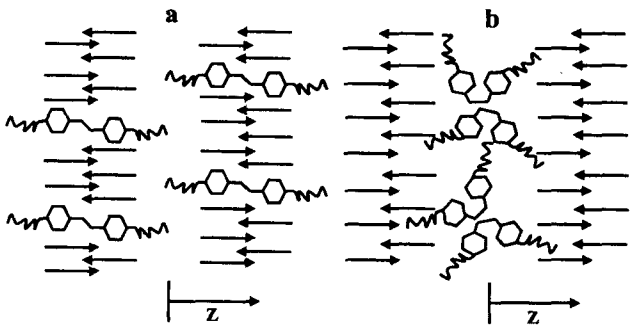
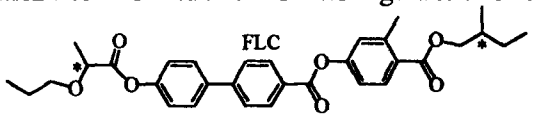


Fig. 8 Schematic representation of the exclusion of *cis*-isomers of azobenzene derivatives from the smectic layers[42].

The observed photomodulation of ferroelectric polarization in ferroelectric smectic C LCs doped with chiral azobenzenes[85,86] has also been attributed to this effect[42]. The *trans*-isomers of the chiral azobenzene are incorporated into the smectic layers contributing to the overall ferroelectric polarization of the material. On *trans-cis* photoisomerization however, the *cis*-isomer is expelled from the layers and their contribution to ferroelectric polarization becomes zero. The possibility of manipulating organic materials at the nanometre scale in this manner can have variety of applications in nanotechnology including development of low-power, high-resolution optical data storage systems[42].

Photochemical switching of alignment in ferroelectric liquid crystals has been extensively investigated by Ikeda and co-workers[85,86]. As discussed above, photoisomerization of azobenzene derivatives doped into ferroelectric LCs results in a decrease in the switching potential of the ferroelectric host (Chart 6).

The working principle of an imaging device, which makes use of this effect, is shown schematically in Fig. 9. The polarization of ferroelectric LC is aligned using an electric field. A weak electric field is then applied in the opposite direction such that it is not sufficient to disturb the polarization of the FLC arrangement due to



12

Azobenzene

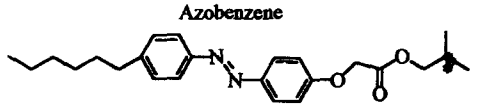


Chart 6

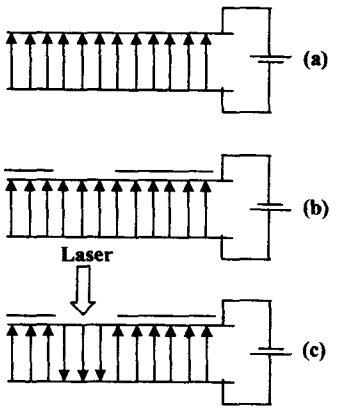
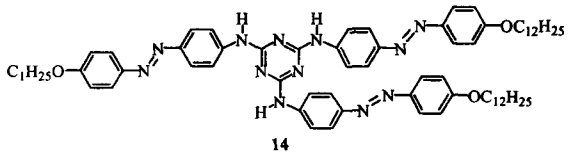


Fig. 9 Schematic representation of photochemical flip of the polarization in ferroelectric LCs doped with azobenzene derivatives (a) Electric field induced alignment of FLC, (b) Application of weaker reverse electric field which maintains the initial polarization, (c) polarization flips due to reduction in threshold voltage caused by the photoisomerization of the azobenzene derivatives[85].

cooperative interaction of LC molecules. On irradiation of selected portions, the threshold voltage for switching drops significantly due to *trans-cis* photoisomerization of the azobezene chromophore, and polarization flips into the opposite direction in these regions.

Photochemically induced phase as well as alignment changes in azobenzene based polymeric LCs have also been used for recording holographic gratings and images. Interference patterns created from coherent laser light at a wavelength absorbed by the polymeric LCs can lead to the formation of gratings due to light-induced phase transitions[87,88], molecular reorientation[89] or mass transport[90]. The use of photoisomerization of azobenzene chromophores in non-LC polymer films, to bring about large-scale mass transport has been reported independently by Natansohn[91] and Tripathy[92]. In these systems the incident interference patterns creates regions with high *trans-cis-trans* isomerization of the azo groups bordered by regions of low isomerization. It has been proposed, that the isomerization process requires free volumes in excess of that which is available in the polymer films resulting in a build up of laser-induced internal pressure. This causes a visco-elastic flow of material from high-pressure to low-pressure regions resulting in the formation of regularly spaced surface relief gratings. Atomic force microscopy revealed that surface profile depths near that of the original film thickness could be obtained. The efficiencies of the gratings could be

significantly enhanced using polymeric LCs. Recently, Wendorff and co-workers have reported on formation of surface relief gratings in a smectic LC, **14** (Chart 7).



14

Chart 7

This compound is isotropic above 270 °C and forms a nematic phase on cooling, which changes to a smectic phase below 221 °C. Irradiation of amorphous optically transparent films of **14** obtained by spin coating from a chloroform solution, using a polarized light beam resulted in the formation of stable gratings. It was observed that the efficiency of the photoinduced grating could be significantly enhanced by heating the sample above its T_g (32 °C). After thermal treatment, the modulation depth of the grating was found to be larger than 400 nm as compared to <5 nm prior to annealing. It has been proposed that annealing the films brings about a migration of the LC molecules due to their tendency to self-organize.

5.2 Surface-Controlled Photoalignment

LCs can be aligned parallel and perpendicular to the cell surface using suitably modified cell surfaces[13,93,94]. If the cell surfaces are modified using photochemically active chromophores, then surface-controlled photoswitching becomes possible. Such surfaces which can be used to switch the alignment of LCs have been termed as 'command surfaces'. Fig. 10 shows a schematic representation of photoswitching in nematic LC cells where surfaces contain immobilized azobenzene derivatives. *Trans-cis* photoisomerization of the immobilized azobenzenes result in switching between the homeotropic and planar alignments[95-97].

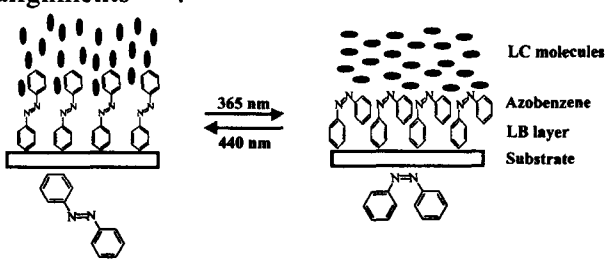
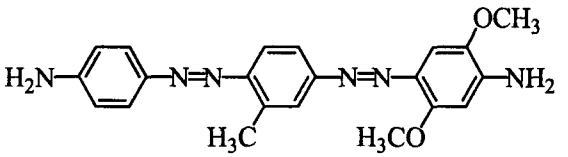


Fig. 10 Schematic illustration of the photochromic reaction-induced alignment changes of nematic LC (command surfaces)[13].

Photoswitching between parallel and perpendicular orientations can also be achieved by irradiation of suitably modified cell surfaces using plane polarized light. Gibbons *et al.* reported photoswitching using cell surfaces coated with a polyimide copolymer doped with a diazodiamine dye, **15** (Chart 8)[98]. The cell used is schematically shown in Fig. 11. One of the surfaces contained the polymer/dye coating while the other surface was coated with the polymer alone.



15

Chart 8

Both surfaces were rubbed with a cloth to provide homogeneous alignment of the nematic LC. On irradiation of the cell with plane polarized light, the nematic LCs close to the surface coated with the dye reorient perpendicular to the plane of polarization of light, while the molecules close to the other side remain unaffected. Thus the irradiated portions acquire a twisted nematic alignment. The irradiated portions can be viewed as images when the cell is placed between crossed or parallel polarizers.

Control of liquid crystal alignment could also be achieved by illuminating the dye-doped polyimide substrate before filling the cell with the nematic LC. Using similar surface controlled optical alignment high-resolution continuous gray scale

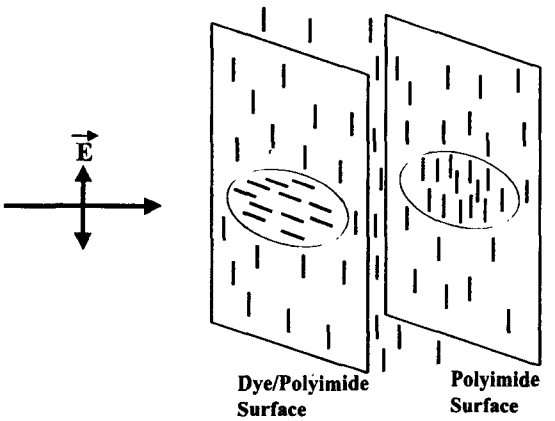


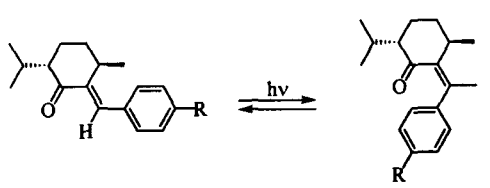
Fig. 11 The geometry of the illuminated liquid-crystal cell. The glass substrates of the cell are not shown for clarity. The rods represent the liquid-crystal orientation near the substrates before and after illumination. The oblong markings represent the illuminated portion[98].

images could also be recorded[99]. This was achieved by focussing the light beam to a size comparable to its wavelength and varying the twist angle of the liquid crystal by varying the polarization direction of the write beam. Varying the polarization of the write beam the orientation of the LC molecules close to the surface coated with dye doped polyimide can be continuously varied from 0-90°, which can provide images with a continuous gray scale when viewed between polarizers. Photoalignment using surfaces modified with chromophores can be fully reversible by irradiation using suitably polarized light.

As with dye-doped LCs, out-of-plane photoalignment of LCs is also possible using such 'command surfaces.' Reversible *cis-trans* photoisomerization of azobenzene side chain attached to vinyl polymers by irradiating them alternately with UV and visible light can bring about reversible out-of-plane alignment of the LC medium[100,101].

6 Photochemical Switching in Cholesteric Liquid Crystals

The pitch of cholesteric LCs is sensitive to temperature, pressure and the presence of dopants[102-105]. From the point of view of photoswitching, it is interesting to note that the pitch of cholesteric LCs is very sensitive to the molecular structure of the dopants. Thus a dopant that can be photochemically switched between two different forms can be utilized to optically switch the pitch of the cholesteric host. Sackman reported on changes in the pitch of cholesteric LCs induced by photoisomerization of azobenzene and stilbene in a mixture of cholesteryl chloride and cholesteryl nonanoate[43]. Photoactive chiral dopants, which can induce cholesteric phases in nematic LCs have also been used to bring about photoinduced pitch changes. For example, (-)-2-arylidene-*p*-menthane-3-ones induce a cholesteric phase when doped into nematic LCs. Photoisomerization of (-)-2-arylidene-*p*-menthane-3-ones (Scheme 3) results in lengthening of the pitch, which is proportional to the extent of photoisomerization[106].



Scheme 3 Photochemical isomerization of (-)-2-arylidene-*p*-menthane-3-one.

Ikeda and co-workers investigated reversible photoinduced pitch changes in nematic LCs doped with a chiral molecule, **16** and photoactive dopant, **17** (Chart 9)[107]. The presence of the chiral dopant induced a cholesteric phase in the nematic LC, while photoisomerization of the azobenzene dopant resulted in a reduction of the pitch of the cholesteric mixture. Blue-shift in the reflectance maximum from 640 to 475 nm was observed.

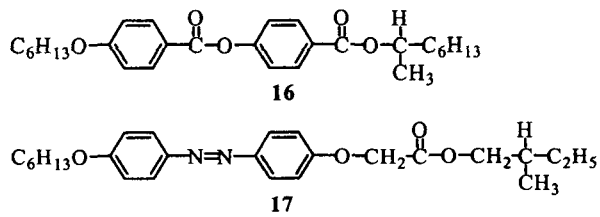


Chart 9

Photoisomerization of the azochromophores in cholesterol-linked azobenzene dopants, **18a,b** (Chart 10) in cholesteric LC mixture consisting of cholesteryl chloride, cholesteryl nonanoate and cholesteryl oleate resulted in elongation of the pitch and associated red-shift in the reflectance band[108].

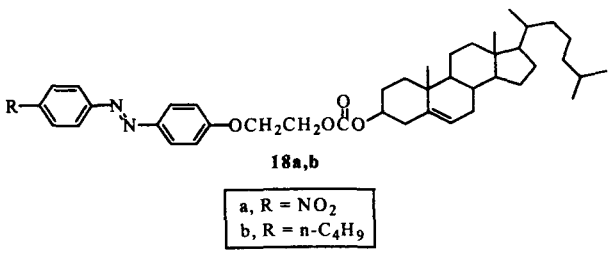


Chart 10

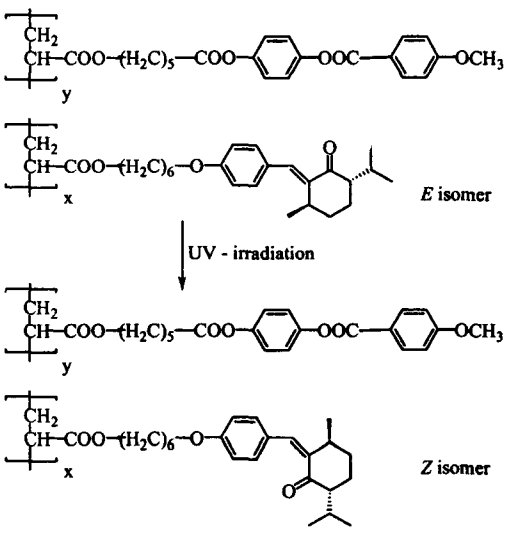
Photoisomerization of **18a** in the cholesteric mixture resulted in a 110 nm red-shift of the reflectance band maximum. In most of the above mentioned studies the change in pitch occurs rapidly and hence under steady-state or constant-wave irradiation conditions the photochemical transformation and change in pitch are indistinguishable. The dynamics of pitch change induced by photoisomerization of the cholesterol-linked azobenzene dopant **18b** in the cholesteric mixture consisting of cholesterol chloride, cholesteryl nonanoate and cholesterol oleate has been studied using time-resolved spectroscopy. The pitch change following isomerization was

found to occur in the time-scale of 80-100 ms[108]. Laser induced heating can also result in temporal changes in the pitch of cholesteric LCs[109]. Pulsed laser irradiation of similar cholesteric mixtures doped with a photochemically inert copper complex which could dump heat following laser excitation, indicated that the reorientation of the LC molecules and change in the pitch, occurred over a time-scale of 300-600 μs[11].

Due to the fluidity of low-molecular weight LCs, their use in long-term storage of photoinduced images is not feasible. In order to try and overcome this problem, photoinduced changes in the pitch have also been investigated in polymeric LCs. Irradiation of a cholesteryl polymer containing the photoactive (-)-2-arylidene-*p*-menthane-3-one as pendants results in elongation of the pitch resulting in a red-shift and broadening of the reflectance band (Scheme 4)[110,111].

The use of polymeric LCs for imaging via photoinduced pitch changes also suffer from several drawbacks including, slow switching times, broadening of the reflectance bands and difficulty in erasure of stored images[112,113].

Tamaoki and co-workers have made elegant use of the glass forming abilities of some cholesteric liquid crystals to overcome the problems associated with photoswitching in low-molecular weight and polymeric LCs[14,114-117]. Glassy liquid crystals can be obtained when the cholesteric phase is solidified by rapid cooling without allowing it to recrystallize, i.e. the macroscopic long-range helical ordering is preserved in the solid state[14]. The glassy materials so obtained retain all the optical characteristics such as selective reflection and selective transmittance of circularly polarized phase. Glassy liquid crystals can also be obtained by polymerizing the cholesteric phase. However in such systems the pitch is not amenable to changes using photochemical transformations. Tamaoki and co-workers have prepared several dicholesteric esters (Chart 11) with molecular weights over 1000 which could be reversibly transformed into glassy and cholesteric LCs both of which showed the iridescent colour characteristic of cholesteric LCs. The stored colour in the glassy state could be tuned by controlling the cooling rate. Glassy LCs could also be obtained by spin-coating the dicholesteryl esters dissolved in dichloromethane.



Scheme 4 Photoisomerization of cholesteric polymer with photoactive (-)-2-arylidene-*p*-menthane-3-one as pendants.

Photoinduced changes in the pitch and fixation of the images could be achieved using azobenzene doped dicholesteryl esters. Thus a thin film of the cholesteric phase of mixture consisting of **19**(n=8) and photochromic azobenzene derivative, **24**(n = 12) (Chart 12) in a 98:2 weight ratio form a red coloured film at 87 °C. Irradiation using 366 nm caused a shift in the reflectance band resulting in blue colouration of the film. Rapid cooling of the film to 0 °C resulted in storage of the photoinduced colour change. The change in colour could be controlled by varying the period of irradiation. The images could be conveniently erased by heating the film above their T_g. The stored images were

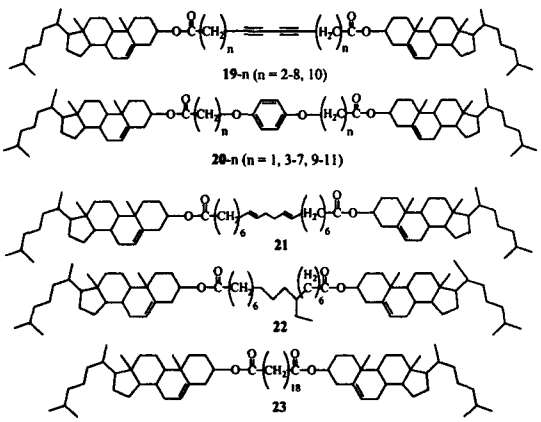
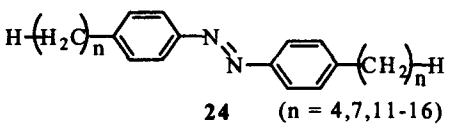


Chart 11



24 (n = 4,7,11-16)

Chart 12

found to be extremely stable (>1 year). These studies have shown the feasibility of developing full-colour rewritable images using both thermal and photochemical modes.

Non-covalent interactions such as hydrogen bonding and metallomesogens containing photoisomerizable azo chromophores capable of forming glassy liquid crystals have also been reported[118,119].

Cholesterol linked azobenzene derivatives have been extensively investigated for their sol-gel formation[120-122], nonlinear optics[123] and use as photoswitching dopants[108]. Recently, Moriyama and Tamaoki have shown that by suitably controlling the nature of the linker between the azobenzene and cholesterol moieties glass forming LCs can be obtained. Imaging in such intrinsically photoactive LC glasses **25, 26** and **27** (Chart 13) have been reported[124].

7 Conclusion

The cooperative interactions and long-range alignment of liquid crystals can result in amplification of weak photochemical transformations, bringing about changes in their bulk properties including isothermal phase transitions, changes in alignment, ferroelectric nature as well as in the pitch of cholesterics. Photochemical reactions of chromophores present as dopants or as an intrinsic part of the LC molecule can be utilized to bring about such transformations. A fine control over these transformations can be achieved by proper selection of the photoactive chromophore as well as by selective use of the various parameters of light such as wavelength, intensity and polarization. The ability of controlling the optical properties of LCs using light makes them potentially useful for a number of photonic applications such as in the development of optical switches, imaging devices, holographic materials, optoelectronics and telecommunications. In view of this, design and study of novel photoresponsive liquid crystalline systems continues to be an active area of research, where efforts are mainly concentrated on improving their response times, resolution and stability.

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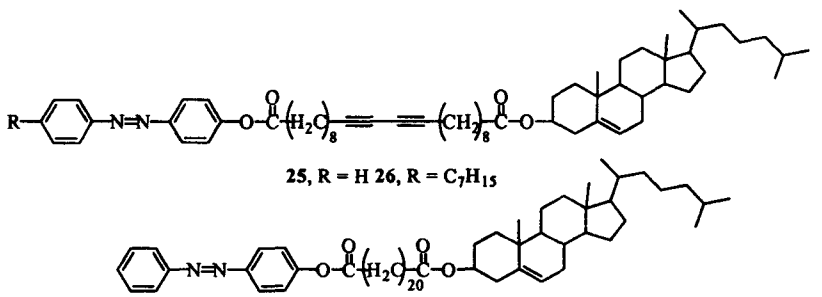

25, R = H **26**, R = C_7H_{15}

27

Chart 13

References

1 *Photochemistry in organized and constrained media* VCH New York (1991)

2 V Ramamurthy and K Venkatesan *Chem Rev* **87** (1987) 433

3 M Ogawa and K Kuroda *Chem Rev* **95** (1995) 399

4 K Kalyanasundaram *Photochemistry in Microheterogeneous Systems* Academic Press New York (1987)

5 K Kalyanasundaram *Chem Soc Rev* **7** (1978) 453

6 D G Whitten, J C Russell and R H Schmehl *Tetrahedron* **38** (1982) 2455

7 K Bhattacharyya PINSA **66** A(2000) 199

8 R G Weiss *Photochemical Processes in Liquid Crystals* (Ed. V Ramamurthy) VCH Publishers New York (1991) 603

9 Y C Lin, B Kachar and R G Weiss *J Am Chem Soc* **111** (1989) 5542

10 V C Anderson, B B Craig and R G Weiss *J Am Chem Soc* **104** (1982) 2972

11 S Das, C Lenoble and R S Becker *J Am Chem Soc* **109** (1987) 4349

12 T Ikeda and A Kanazawa *Molecular Switches* Wiley-VCH Weinheim (2001)

13 K Ichimura *Chem Rev* **100** (2000) 1847

14 N Tamaoki *Adv Mater* **13** (2001) 1135

15 D Demus *Liquid Crystals-Applications and Uses* World Scientific Singapore **1** (1995)

16 S Chandrasekhar *Liquid Crystals* Cambridge University Press Cambridge (1977)

17 H Kelker and R Hatz *Hand book of liquid crystals* Verlag Chemie Weinheim (1980)

18 P G Gennes *The Physics of Liquid Crystals* Oxford Clarendon (1974)

19 D Demus and L Richter *Texture of Liquid Crystals* Weinheim New York (1978)

20 G W Gray and J W Goodby *Smectic Liquid Crystals* Leonard Hill Glasgow London and Heyden & Son Philadelphia (1984)

21 G H Brown *Advances in Liquid Crystals* Academic Press New York San Francisco London **1-6** (1983)

22 A Blumstein *Polymeric Liquid Crystals* Plenum New York (1985)

23 D Demus *Liq Cryst* **5** (1989) 75

24 B Wunderlich, M Moller and H G Wiedemann *Mol Cryst Liq Cryst* 140 (1986) 211

25 L Pohl and U Finkenzeller *Liquid Crystals - Applications and Uses* (Ed. B Bahadur) World Scientific Singapore **1** (1995) 139

26 P Palffy-Muhoray *Liquid Crystals-Applications and Uses* (Ed. B Bahadur) World Scientific Singapore **1** (1995) 493

27 T Scheffer and J Nehring *Liquid Crystals-Applications and Uses* (Ed. B Bahadur) World Scientific Singapore **1** (1995) 231

28 B Bahadur *Liquid Crystals-Applications and uses* World Scientific Singapore **1-3** (1995)

29 F Kahn *Appl Phys Lett* **22** (1973) 111

30 K Nakamura, Y Oda and M Sugimoto *J Appl Phys* **59** (1986) 593

31 S E Shields and W P Bleha *Liquid Crystals-Applications and Uses* World Scientific Singapore **1** (1995) 437

32 V P Shibaev, S G Kostromin, N A Plate, S A Ivanov, V Y Vetrov and I A Yakovlev *Polym Commun* **24** (1983) 364

33 H J Coles and R Simon *Polymer* **26** (1985) 1801

34 T Urabe, K Arai and A Ohkoshi *J Appl Phys* **54** (1983) 1552

35 W Haas, J Adams and J Wysocki *Mol Cryst Liq Cryst* **7** (1969) 371

36 M Emmelius, G Pawlowski and H W Vollman *Angew Chem Int Ed Engl* **28** (1989) 1445

37 I Cabrera, M Engel, L Haübling, C Mertisdorf and H Ringsdorf *Photoinduced Structural Changes in Organized Supramolecular Systems Frontiers in Supramolecular Organic Chemistry and Photochemistry* (Eds. H Schneider and H Dürr) Weinheim New York (1991)

38 H Ringsdorf, I Carbrera and A Dittrich *Angew Chem Int Ed Engl* **30** (1991) 76

39 M Suarez and G B Schuster *J Am Chem Soc* **117** (1995) 6732

40 M Zhang and G B Schuster *J Org Chem* **59** (1994) 1855

41 T Ikeda and O Tsutsumi *Science* **268** (1995) 1873

42 Y Lansac, M A Glaser, N A Clark and O D Lavrentovich *Nature* **398** (1999) 54

43 E Sackman *J Am Chem Soc* **93** (1971) 7088

44 T Kobayashi, E O Degenkolb and P M Rentzepis *J Phys Chem* **83** (1979) 2431

45 S Kurihara, T Ikeda and S Tazuke *Mol Cryst Liq Cryst* **178** (1990) 117

46 T Ikeda, T Miyamoto, S Kurihara and S Tazuke *Mol Cryst Liq Cryst* **188** (1990) 223

47 T Ikeda, T Miyamoto, S Kurihara and S Tazuke *Mol Cryst Liq Cryst* **188** (1990) 235

48 T Ikeda, T Miyamoto, S Kurihara, M Tsukada and S Tazuke *Mol Cryst Liq Cryst* **182B** (1990) 357

49 S Kurihara, T Ikeda, T Sasaki, H-B Kim and S Tazuke *Mol Cryst Liq Cryst* **195** (1991) 251

50 S Kurihara, T Ikeda, T Sasaki, H-B Kim and S Tazuke *J Chem Soc Chem Commun* (1990) 1751

51 C Denekamp and B L Feringa *Adv Mater* **10** (1998) 1080

52 K S Burnham and G B Schuster *J Am Chem Soc* **121** (1999) 10245

53 A Shishido, O Tsutsumi, A Kanazawa, T Shiono and T Ikeda *J Phys Chem B* **101** (1997) 2806

54 A Shishido, O Tsutsumi, A Kanazawa, T Shiono, T Ikeda and N Tamai, *J Am Chem Soc* **119** (1997) 7791

55 O Tsutsumi, T Shiono, T Ikeda and G Galli *J Phys Chem B* **101** (1997) 1332

56 T Kato, N Hirota, A Fujishima and J M J Frechet *J Polym Sci A Polym Chem* **34** (1996) 57

57 V A Mallia, M George and S Das *Chem Mater* **11** (1999) 207

58 V A Mallia and S Das *Liq Cryst* **28** (2001) 259

59 R Brettle, D A Dunmur, N J Hindle and C M Marson *J Chem Soc Chem Commun* (1992) 411

60 R Brettle, D A Dunmur, N J Hindley and C M Marson *J Chem Soc Perkin Trans 1* (1993) 775

61 R Davis, V A Mallia and S Das *Chem Mater* **15** (2003) 1057

62 B Dellinge and, M Kasha *Chem Phys Lett* **38** (1976) 9

63 Y-P Sun, J Saltiel, E A Hoburg and D Waldeck *J Phys Chem* **53** (1991) 10336

64 R S H Liu, A E Asato and M Denny *J Am Chem Soc* **105** (1983) 4829

65 R S H Liu *Acc Chem Res* **34** (2001) 555

66 J Michl and E W Thulstrup *Spectroscopy and Polarized Light* VCH New York (1995) pp 198

67 M Dumont *Mol Cryst Liq Cryst* **282** (1996) 437

68 A Sekkat and M Dumon *Synth Met* **54** (1993) 373

69 Z Sekkat, J Wood and W Knoll *J Phys Chem* **99** (1995) 17226

70 D Hore, A Natansohn and P Rochon *Can J Chem* **76** (1998) 1684

71 F Jones and T J Reeve *J Soc Dyers Col* (1979) 352

72 F Jones and T J Reeve *Mol Cryst Liq Cryst* **60** (1980) 99

73 A Y Bobrovsky, A A Pakhomov, X-M Zhu, N I Boiko, V P Shibaev and J Stumpe *J Phys Chem B* **106** (2002) 540

74 S Morino, A Kaiho and K Ichimura *Appl Phys Lett* **73** (1998) 1317

75 J Stumpe, T Geue, T Fischer, H Menzel *Thin Solid Films* (1996) 606

76 T Fischer, L Lasker, J Stumpe and S Kostromin *J Photochem Photobiol A Chem* **80** (1994) 453

77 L Lasker, J Stumpe, T Fischer, L Rutloh, S Kostromin and R Ruhmann *Mol Cryst Liq Cryst* **261** (1995) 371

78 L Lasker, T Fischer, J Stumpe, S Kostromin, S Ivanov, V P Shibaev and R Ruhmann *Mol Cryst Liq Cryst* **253** (1994)1

79 Y Wu, Y Demachi, O Tsutsumi, A Kanazawa, T Shiono and T Ikeda *Macromolecules* **31** (1998) 349

80 S Bartkiewics and A Miniewics *Adv Mater Opt Electron* **6** (1996) 219

81 S Bartkiewics, A Januszko, A Miniewics, J Parka *J Pure Appl Opt* **5** (1996) 799

82 N Yoshimoto, S Morino, A Kaiho and K Ichimura *Chem Lett* (1999) 711

83 W R Folks, Y A Reznikov, S N Yarmolenko and O D Lavrentovich *Mol Cryst Liq Cryst* **292** (1997) 183

84 T A Krentsel, O D Lavrentovich and S Kumar *Mol Cryst Liq Cryst* **320** (1998) 77

85 T Sasaki, T Ikeda and K Ichimura *J Am Chem Soc* **116** (1994) 625

86 T Ikeda, T Sasaki and K Ichimura *Nature* **361** (1993) 428

87 T Yamamoto, M Hasegawa, A Kanazawa, T Shiono and T Ikeda *J Mater Chem* **10** (2000) 337

88 T Yamamoto, M Hasegawa, A Kanazawa, T Shiono and T Ikeda *J Phys Chem B* **103** (1999) 9873

89 M Eich and J Wendorff *J Opt Soc Am B* **7** (1990) 1428

90 A Stracke, J H Wendorff, D Goldmann, D Janietz and B Stiller *Adv Mater* **12** (2000) 282

91 C J Barrett, A L Natansohn and P L Rochon *J Phys Chem B* **100** (1996) 8836

92 D Y Kim and S K Tripathy *Appl Phys Lett* **66** (1995) 136

93 N Kawatsuki, H Ono, H Takatsuka, T Yamamoto and O Sangen *Macromolecules* **30** (1997) 6680

94 M Schadt, H Seiberle and A Schuster *Nature* **381** (1996) 212

95 K Ichimura, Y Suzuki, T Seki, A Hosoki, K Aoki *Langmuir* **4** (1988) 1214

96 K Ichimura, Y Suzuki, T Seki, A Kawanishi, K Aoki *Macromol Chem Rapid Commun* **10** (1989) 5

97 T Seki, M Sakuragi, A Kawanishi, T Tamaki, R Fukuda and K Ichimura *Langmuir* **9** (1993) 211

98 W M Gibbons, P J Shannon, S T Sun and B J Swetlin *Nature* **351** (1991) 49

99 W M Gibbons, T Kosa, P Palffy-Muhoray, P J Shannon, S T Sun and B J Swetlin *Nature* **377** (1995) 43

100 K Aoki, T Seki, Y Suzuki, T Tamaki, A Hosoki and K Ichimura *Langmuir* **8** (1992) 1007

101 Y Kawanishi, T Tamaki, M Sakuragi, T Seki, Y Suzuki and K Ichimura *Langmuir* **8** (1992) 2601

102 J L Fergason *Appl Opt* **7** (1968) 1729

103 J L Fergason *Sci Am* **211** (1964) 76

104 J H Muller *Mol Cryst* **2** (1966) 167

105 P N Keating *Mol Cryst Liq Cryst* **8** (1969) 315

106 S N Yarmolenko, L A Kutulya, V V Vashchenko and L V Chepeleva *Liq Cryst* **16** (1994) 877

107 H-K Lee, K Doi, H Harada, O Tsutsumi, A Kanazawa, T Shiono and T Ikeda *J Phys Chem B* **104** (2000) 7023

108 M George, V A Mallia, P K S Antharjanam, M Saminathan and S Das *Mol Cryst Liq Cryst* **350** (2001) 125

109 R S Becker, S Chakravorti and S Das *J Chem Phys* **90** (1989) 2802

110 M Brehmer, J Lub and P V D Witte *Adv Mater* **10** (1998) 17

111 P V D Witte, J C Galan and J Lub *Liq Cryst* **24** (1998) 819

112 A Y Bobrovski, N I Boiko, V P Shibaev and J Spriger **12** (2000) 16

113 A Y Bobrovski, N I Boiko and V P Shibaev **25** (1998) 679

114 N Tamaoki, M Moriyama and H Matsuda *Angew Chem Int Ed Engl* **39** (2000) 509

115 N Tamaoki, A V Parfenov, A Masaki and H Matsuda *Adv Mater* **9** (1997) 1102

116 N Tamaoki, G Kruk and H Matsuda *J Mater Chem* **9** (1999) 2381

117 N Tamaoki, S Song, M Moriyama and H Matsuda *Adv Mater* **12** (2000) 94

118 V A Mallia, P K S Antharjanam and S Das *Chem Lett* (2001) 752.

119 P K S Antharjanam, V A Mallia, S Das *Chem Mater* **14** (2002) 2687

120 H Kawabata, K Murata, T Harada and S Shinkai *Langmuir* **11** (1995) 623

121 K Murata, M Aoki and S Shinkai *Chem Lett* (1992) 739

122 K Murata, M Aoki, T Suzuki, T Harada, H Kawabata, T Komori, F Ohseto, K Ueda and S Shinkai *J Am Chem Soc* **116** (1994) 6694

123 M George and S Das *Chem Lett* (1999) 1081

124 M Moriyama and N Tamaoki *Chem Lett* (2001) 1142.