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Liquid crystal-based actuators

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Liquid crystal polymer networks (LCNs) have a great potential in soft actuator technologies. In contrast to other materials, LCNs offer a wide range of external stimuli which can trigger their actuation. These are for example based on changes of temperature, photo-induced or *via* the application of electric fields. We here discuss the main LCN actuation mechanisms and classify them into several groups based on the used stimulus. Specific recent examples are provided for liquid crystal actuators and several general applications of such materials in connection to actuation mechanisms are exemplary outlined.
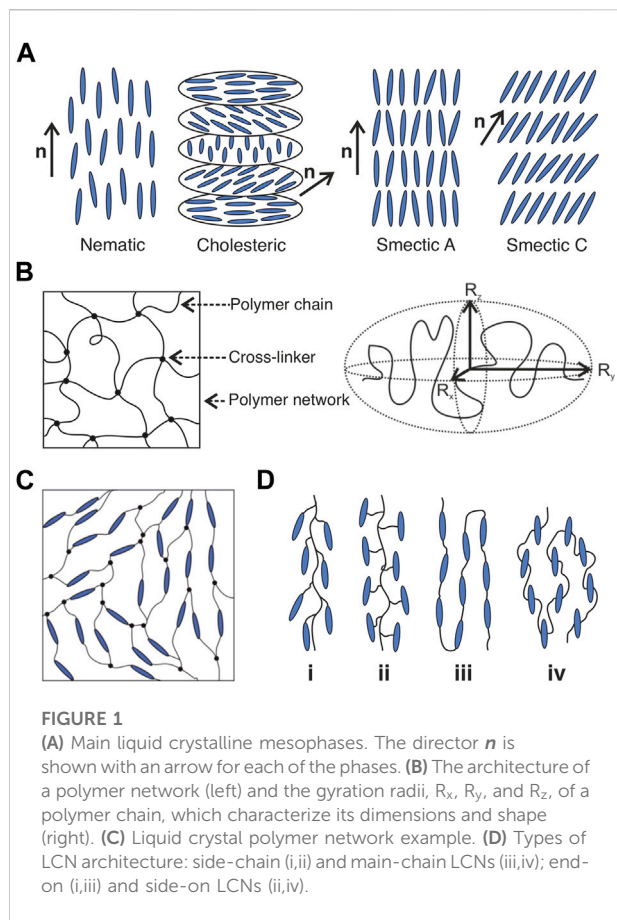
1 Introduction

Liquid crystals (LCs) are unique materials with an unusually rich phase diagram. Due to the anisotropic shape of their molecules (e.g., rod-like, disk-like), liquid crystals do not directly transition between the liquid and solid states, but go through one or several additional phases called liquid crystalline mesophases. Being in one of these states, matter exhibits properties of both liquids and solids: molecules can move freely, enabling a liquid-like flow; while at the same time their orientation is correlated, leading to the long-range orientational order observed in solids. Additionally, liquid crystals can exhibit low-dimensional positional order (1D—fluid smectics; 2D—hexatic smectics). Liquid crystalline mesophases differ in the type of orientational order and the order of the molecules' centres of mass (Figure 1A). For example, in the nematic phase (N) on small scales molecules are oriented in the same direction on average, while there is no order in the positions of the centres of mass. Another very similar example is the cholesteric phase (N*), which is the chiral version of the nematic phase, the asterix "*" indicating chirality of the system, which often manifests itself through a helical superstructure. Similar to the nematic phase, the cholesteric molecules on small distances order parallel, but on larger scales they tend to form spiral structures, while the centre's of mass exhibit no positional order. The fluid smectic state is also relatively similar to the nematic phase, but here this phase shows a long-range one-dimensional order of the centres of mass as the molecules are arranged in layers. The LC molecules can be parallel to the layer's normal—the smectic A phase—or tilted relative to it—the smectic C phase. A number of other mesophases exist, information about which can be found in (Chandrasekhar, 1992; Stegemeyer, 1994; de Gennes and Prost, 1995; Blinov, 2011; Goodby et al., 2014; Collings and Goodby, 2019).

Liquid crystals are well known for their applications in display technologies (Lueder, 2010; Chen, 2011). The aim to improve display performance has been dictating the

FIGURE 1
(A) Main liquid crystalline mesophases. The director **n** is shown with an arrow for each of the phases. **(B)** The architecture of a polymer network (left) and the gyration radii, R_x, R_y, and R_z, of a polymer chain, which characterize its dimensions and shape (right). **(C)** Liquid crystal polymer network example. **(D)** Types of LCN architecture: side-chain (i,ii) and main-chain LCNs (iii,iv); end-on (i,iii) and side-on LCNs (ii,iv).

direction of LC research for many years. These efforts have resulted in LCD screens being integrated in numerous devices (Kawamoto, 2012). However, nowadays they start to be gradually replaced by the new, more efficient technology of organic light-emitting diodes (OLED) (Tsujimura, 2017). Therefore, other areas of LC research like biosensors (Luan et al., 2020), active matter (Zhang et al., 2021), optical devices (Jaroszewicz and Bennis, 2020), and soft actuators (Ula et al., 2018) started to attract more interest, promising new applications in the future.

This review is focused on liquid crystals in the context of actuators, devices which transform supplied energy into motion and changes of their shape. All actuators can be divided into two types: rigid and soft. The former, based on servomotors and MEMs (micro–electro–mechanical systems), are well developed and used widely (in robotic manipulators on factories and building sites, microphones, scanning probe microscopes, etc.). At the same time, soft actuator technologies, based on soft and active materials (polymers, liquid crystals, colloids, shape memory alloys, etc.), only start to be actively investigated. This type of actuators is expected to provide several advantages over the rigid ones, such as smooth, complex, animal-like motions, a variety of external triggering stimuli that can be used as an energy source, a high adaptability

to environment changes, biocompatibility as well as the possibility of the low-effort creation of sub-centimetres actuators (El-Atab et al., 2020). Applications in artificial muscles (Thomsen et al., 2001; Ambrogi et al., 2005), waste energy harvesting (Wei et al., 2018; Han et al., 2020), microfluidics (Chen et al., 2011, 2010; Lv et al., 2016), and soft robotics (Chang et al., 2021) are possible.

Among the materials used in soft actuator technologies, liquid crystal polymer networks play an important role because of the great variety of actuation-triggering stimuli. Except for few examples (Cheng et al., 2015; Lv et al., 2016), they are the only material used for liquid crystal-based actuators. That is the reason why this review is mainly concentrated on such materials. We will first explain the nature of LCNs and then discuss different mechanisms of their actuation, classifying them by the used external stimulus.

2 Liquid crystal polymer networks

Liquid crystal polymer networks (Warner and Terentjev, 2003; de Jeu, 2012) are polymer networks (Figure 1B, left) with incorporated liquid crystal (or mesogenic) moieties (Figure 1C). Their existence was predicted by de Gennes in 1975 (de Gennes, 1975), while they were first synthesized by Finkelmann in 1981 (Finkelmann et al., 1981). The unique property of such systems is that the average orientation of mesogenic units, characterised by the vector **n** (called the director) (Figure 1A) (Chandrasekhar, 1992; de Gennes and Prost, 1995; Collings and Goodby, 2019), and the conformation of polymer chains, characterized by the radii of gyration (Figure 1B, right) (Rubinstein and Colby, 2003), are interrelated: polymer chains are elongated in a certain direction (often parallel or perpendicular) relative to LC units, which depends on the network's chemical constitution and architecture. Moreover, a change in the orientation of one of them often causes a change in the orientation of another. As will be shown below, these properties, in combination with the stability of LCNs, caused by the cross-linking of polymer chains, allows one to use them as materials for actuators.

LCNs can be divided into liquid crystal elastomers (LCEs) and liquid crystal thermosets (LCTs, or duromers, or liquid crystal polymer networks as they are often referred to), which are lightly and highly cross-linked, respectively. Due to higher elasticity, enabling relatively large deformations, LCEs are more often investigated in the context of actuator technologies. Nevertheless, LCTs can also be used for this purpose.

The properties of building blocks used for the synthesis of LCNs (i.e., monomers, cross-linkers, mesogenic units, spacers), and the way the blocks are combined with each other significantly influence the liquid crystalline and mechanical properties of the networks and can be used to tune them. For example, mesogenic units determine the nature of liquid
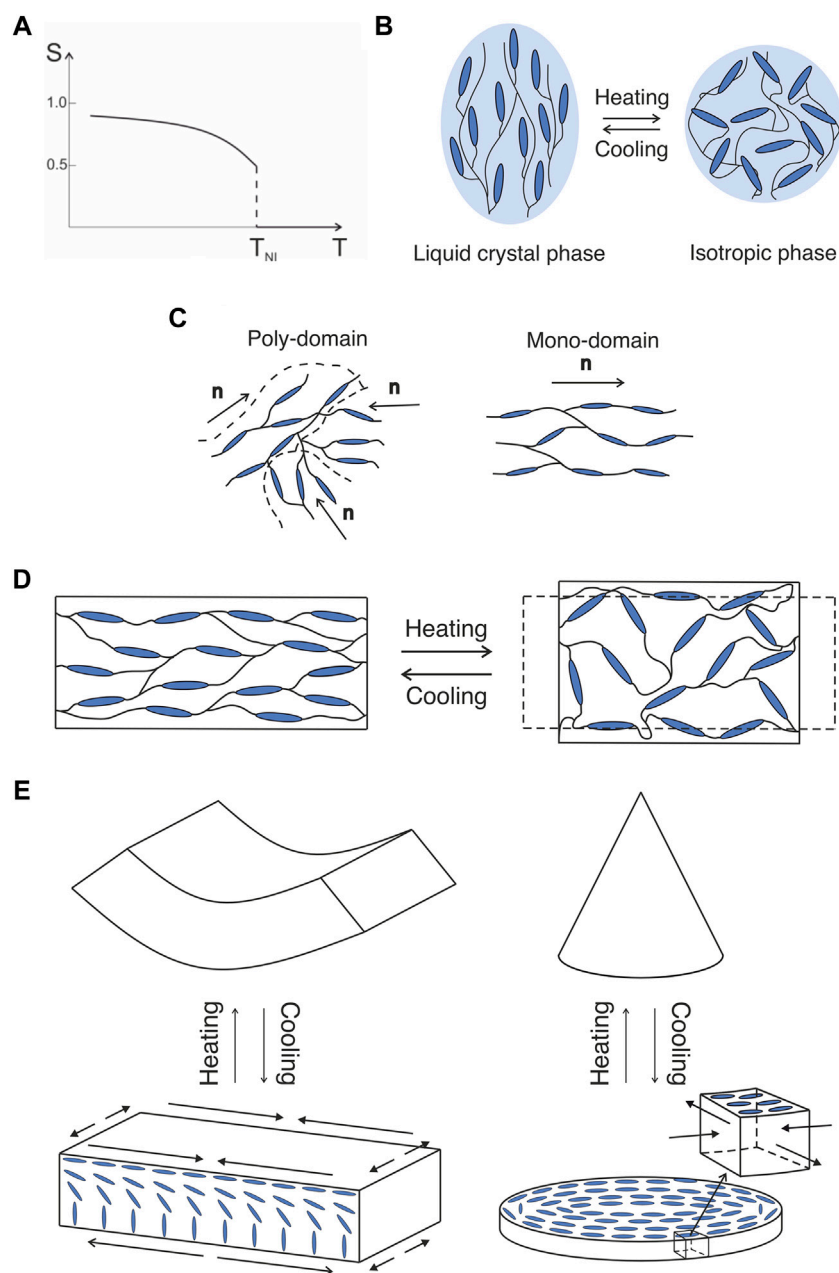
FIGURE 2
(A) Temperature dependence of the order parameter S. **(B)** Schematic illustration of the thermally induced deformation of an LCN's small element. **(C)** Schematic illustration of poly-domain and mono-domain LCNs. **(D)** Schematic illustration of the macroscopic, thermally induced deformation of a mono-domain LCN. **(E)** Bending of an LCN film with the so-called splay alignment (left) occurring due to the thermally induced contraction of its top side and elongation of the bottom side along the same direction (the elongation of the sides in the orthogonal direction does not contribute to the bending). Transformation into a cone for an LCN film with a concentric alignment with a +1 defect in the centre (right) occurring due to the thermally induced material expansion along the radial directions and contraction along the tangential directions. Polymer chains and changes in the thickness of the films are not shown.

crystallinity of an LCN: thermotropic for rod- (Finkelmann et al., 1981) and disk-like (Kreuder et al., 1985) mesogens and less conventional lyotropic for amphiphilic mesogens (Löffer and Finkelmann, 1990) (lyotropic LCs (Neto and Salinas, 2005; Dierking and Martins Figueiredo Neto, 2020) exist in a certain range of LC unit concentrations instead of temperature ranges). The way mesogenic units are incorporated into a polymer network also plays an important

role since it can determine the mesophase type. For example, LCNs can be divided into end-on LCNs (Figures 1Di,iii), for which LC units are connected with main- or side-chains of a polymer network along their long axis (for rods), and side-on LCNs (Figures 1Dii,iv), for which the connection is lateral. Notably, the former often form smectic phases (Brehmer et al., 1994; Nishikawa et al., 1997), while for the latter the nematic phase is more common (Thomsen et al., 2001). LCNs can also be divided into side-chain (Figures 1Di,ii) and main-chain (Figures 1Diii,iv) LCNs, depending on the LC units' location in the network. Using monomers with chiral mesogens attached as side-chains helps to synthesise LCNs exhibiting the cholesteric and chiral smectic phases (Finkelmann et al., 1981; Zentel et al., 1987; Zentel, 1988; Kim and Finkelmann, 2001). The cross-linking density and the length of spacers which attach mesogens to main-chains in case of side-chain LCNs allow one to control the stiffness of the material (Kupfer et al., 1994). The creation of self-repairable systems is possible if special cross-linkers are used (Wang et al., 2017). There are numerous other ways to tune LCNs' properties via their chemical design. Detailed information about them can be found in (Brömmel et al., 2012; Kularatne et al., 2017; Herbert et al., 2021).

Further, nematic LCNs will be used for the discussion and denoted just as LCNs, unless stated otherwise. However, almost all mechanisms can be realised in other LC phases as well.

3 Thermally induced actuation

Thermally induced actuation is based on the temperature dependence of the LCN order parameter,

$$S = \frac{1}{2} \langle 3 (\cos \Theta)^2 - 1 \rangle$$

where Θ is an angle between an LC molecule and the director $\boldsymbol{n}$, $< >$ is an average over ensemble and time, and S characterizes the degree of order in the orientation of LC units (Figure 2A) (Chandrasekhar, 1992; de Gennes and Prost, 1995; Collings and Goodby, 2019). The decrease in the order with increasing temperature (caused by thermal motion of LC molecules) leads to a decrease in the elongation of polymer chains. This, in turn, causes the contraction of the LCN along the former direction of the chain elongation and, assuming the conservation of volume, an elongation along directions perpendicular to it. Maximum shape changes occur at the temperature of the nematic-isotropic phase transition, T_{NI}, at which the system completely loses its liquid crystalline properties and undergoes a 1st order discontinuous transition to the isotropic phase (Figure 2B). The deformations are reversible and can be recovered by cooling the LCN.

However, the director is uniform only on a relatively small scale, inside domains into which a sample appears to be

spontaneously split (Figure 2C, left). In this case, the LCN is called a poly-domain liquid crystal network. In the poly-domain state, domain shape changes do not result in the shape change of the whole network. In order to obtain a macroscopic deformation (Figure 2D), one needs to uniformly align LC units across the sample (Figure 2C, right), i.e., to prepare a mono-domain liquid crystal network. There are several alignment techniques used for this purpose, including mechanical stretching of a sample (Kupfer and Finkelmann, 1991), preparation in traditional LC cells with alignment layers (Thomsen et al., 2001), the alignment of LC units with magnetic (Buguin et al., 2006) or electric (Brehmer et al., 1994) fields, and others.

Controlled alignment patterning, which may be useful for some applications, can be achieved via the ink-jet printing technique (Gantenbein et al., 2018; Kotikian et al., 2018), by using LC cells with patterned alignment layers (Ware et al., 2016), and some other methods and results in more complex deformations, which often involve the 3D folding of a sample. Several examples of non-uniform LC units' arrangements and corresponding thermally induced shape changes are shown in Figure 2E.

More information on alignment techniques can be found in comprehensive reviews by Kularatne et al. (2017) and Herbert et al. (2021). It should be noted that a predesigned LC molecules' orientation is necessary for all mechanisms of LCN actuation and is realized using the same techniques mentioned above. Further, all discussed LCN systems will be mono-domain, unless stated otherwise.

Next, we will investigate different methods of changing the LCN's temperature, which allow one to use the actuation mechanism for various purposes.

3.1 Heating through thermal conduction

The simplest way to change the temperature of an LCN is to put it in a contact with an object of a different temperature. Choosing the environment as the object can be very beneficial as it allows one to create environmentally responsive and adaptive actuators. Such qualities can be used for biomedical applications, e.g., drug release systems (Jampani et al., 2018), low-grade waste heat harvesting (Han et al., 2020) and self-controlled technologies. However, from a technical point of view, it is difficult to use the thermal conduction method to perform a controlled actuation process, which can be desirable for applications in soft robotics. One of the approaches to overcome this problem, suggested by He et al. (2019a) and He et al. (2020), is the integration of water channels inside an LCN sample and channelling water of a desired temperature through the device. The authors demonstrated the feasibility of their actuator by animating an artificial skeleton (Figure 3A) (He et al., 2019b). However, the implementation of such a mechanism in technologies is still challenging, since it needs a water
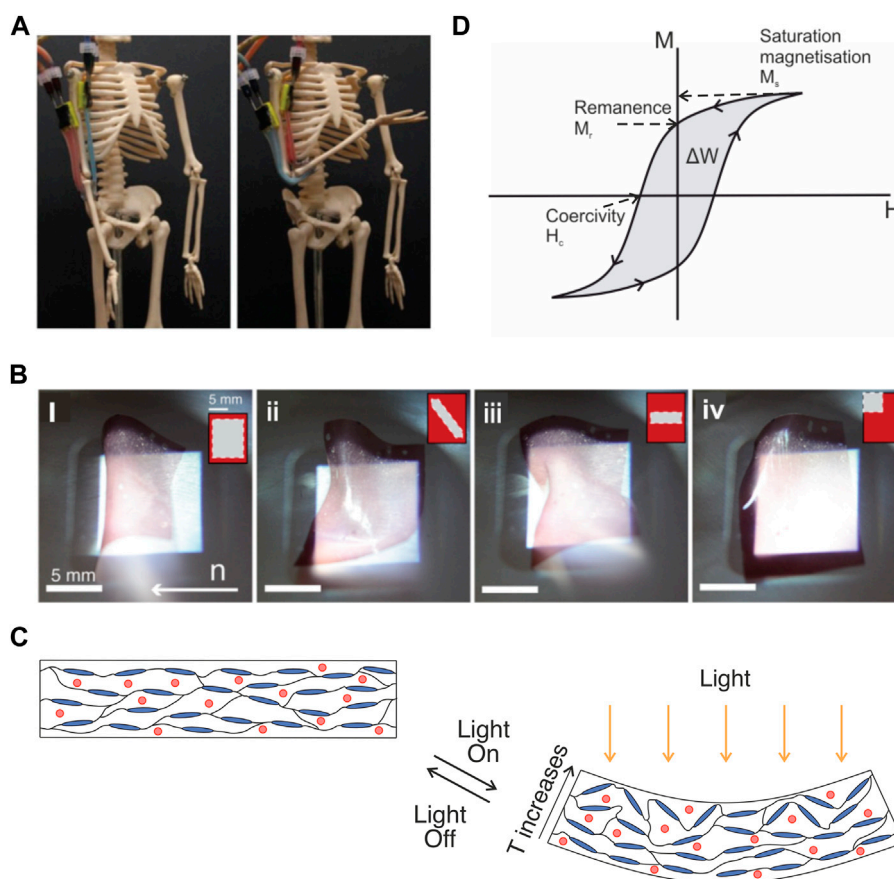
FIGURE 3
(A) Arm bending by the contraction of biceps muscle and the elongation of triceps muscle made of mono-domain LCN films with integrated water channels. Reprinted with permission from He et al. (2019a). Copyright 2019 John Wiley and Sons. **(B)** LCN film deformations (i, ii, iii, iv) caused by irradiation with different VIS light patterns indicated in the top right corners (grey zones correspond to illuminated areas). The film bends due to the finite penetration of light into the LCN material which will be discussed further in the text. Reprinted with permission from Hauser et al. (2016). Copyright 2016 American Chemical Society. **(C)** Photo-thermally induced bending of a mono-domain LCN film caused by a finite light penetration depth. **(D)** Magnetic field strength dependence of magnetisation in case of a hysteresis.

temperature control system, which is difficult to make compact enough. That is why other, semi-thermal methods, which still allow the use of the thermally induced actuation mechanism, are necessary.

3.2 Photo-induced heating

Light can be employed to heat LCN if one introduces photo-thermal agents into the material (Dong and Zhao, 2018), which can convert light energy to thermal energy. Graphenes (Wei et al., 2016), carbon nanotubes (CNTs) (Ji et al., 2010; Camargo et al., 2011), metal nanoparticles (Sun et al., 2012; Hauser et al., 2016), dyes (de Haan et al., 2012; Guo et al., 2016; Gelebart et al., 2017; Liu L et al., 2017; Qin et al., 2020), and conjugated polymers (Liu et al., 2016) often serve as dopants due to their high light absorption and quantum yield of photo-thermal energy conversion for certain wavelengths (Dong and Zhao, 2018). Graphenes, CNTs, and metal nanoparticles are efficient at absorbing both visible (VIS) and near-infrared (NIR) light, while dyes are more specific (for instance, Lumogen IR788 (de Haan et al., 2012) and Dye 1002 (Kohlmeyer and Chen, 2013) are for NIR light; ABS407, ABS594, and ABS694 dyes (Qin et al., 2020) are for VIS light). Conjugated polymers are used for NIR light-responsive actuators.

This heating mechanism allows to control the actuation remotely (Dong and Zhao, 2018). This property can be employed in devices which work in dangerous conditions, e.g., in toxic environments or under high pressure. The creation of light-responsive actuators is possible and can be used, for example, in devices which monitor light conditions or light-harvesting technologies (Wei et al., 2018). Considering the fact

that NIR light has a relatively high tissue penetration depth, and both VIS and NIR light are not harmful for biological systems, the discussed photo-thermal effect can also be used for bio-medical applications, e.g., telerobotic surgery. Another advantage is the possibility of a high-precision spatial control of light intensity, which allows one to perform shape deformations more complex than a simple contraction/elongation (Dong and Zhao, 2018) as was demonstrated by Hauser et al. (2016) (Figure 3B).

However, the photo-induced heating techniques encounter some challenges as well. Photo-thermal dopants are usually only poorly dispersible in LCNs, and thus achieving high concentrations, necessary to speed up switching-on actuation times, is often difficult and demands a special treatment of dopants. Additionally, high concentrations of dopants can make LCNs stiffer and in this way restrict deformation magnitudes. It also has to be taken into account that in the beginning of the irradiation process, a temperature gradient forms inside an LCN sample due to the finite light penetration depth. For a homogeneous film sample (i.e., n is uniform and parallel to the LCN film plane), it results in a stronger contraction of the film side exposed to light. This in turn leads to its bending, which can be both desirable and undesirable (Figure 3C), depending on application. A comprehensive analysis of photo-thermally induced actuators can be found in (Dong and Zhao, 2018).

3.3 Electrically induced heating

The Joule heating effect can also be realised in LCN systems. For this purpose, conductive wires (Spillmann et al., 2007a; Petsch et al., 2014), layers (Greco et al., 2012), and nanoparticles (Chambers et al., 2009), channels filled with liquid metals (Kotikian et al., 2021), and liquid metal droplets (Ford et al., 2019; Kent et al., 2020; Ambulo et al., 2021) are added to LCNs. Using electricity to heat LCNs allows one to easily combine actuators with well-developed electronic technologies. However, for this approach heat transfer is often not efficient enough, while the incorporation of the external objects into LCNs often leads to the materials' stiffening and relatively quick degradation due to the incompatibility of the objects with the LCNs. Furthermore, the degradation is also caused by large temperature gradients present in the system (Chambers et al., 2009).

3.4 Magnetically induced heating

In the presence of an alternating magnetic field (AMF) of a high enough frequency, the changes in the field and the magnetic dipole orientation of a ferromagnetic material can be not synchronised, leading to hysteresis (Figure 3D). Then, after one traversal, the work the magnetic field does on the system of a unit volume is

$$\Delta W = -\mu_0 \int M \cdot dH > 0$$

where H is the magnetic field strength, M is the magnetisation and μ_0 is the vacuum permeability. Hence the internal energy of the system should increase leading to an increase in its temperature (Dennis and Ivkov, 2013; Dutz and Hergt, 2013). From this follows the idea to add magnetic nanoparticles to LCNs in order to magnetically induce LCN heating (Kaiser et al., 2009; Winkler et al., 2010).

The advantage of this mechanism is the remote control of actuation. Moreover, AMFs with radio frequencies can be employed, which makes this heating mechanism very attractive in medicine. Biological tissues are mostly transparent for radio AMFs and so will not be heated by the fields (Dennis and Ivkov, 2013; Dutz and Hergt, 2013), while an actuator placed in a human body will be able to accept the signal. However, one can again expect problems related to the poor compatibility of the external objects with LCNs.

4 Photo-induced actuation

It is possible to induce the LC-isotropic phase transition without heating an LCN if photosensitive molecules, having rod-like and bent isomers, (most often azobenzene derivatives) are present in the system. While the molecules are in their extended rod-like form [called the trans-form for azobenzene derivatives (Figure 4C, left)], they stabilize liquid crystalline order in the LCN (Figure 4B, left). But if the sample is irradiated by light of a certain wavelength, these groups absorb photons and change their conformation to a bent form [the cis-form for azobenzene derivatives (Figure 4C, right)]. In this state, the molecules act like impurities and decrease the LC-isotropic transition temperature and thus lowering the degree of liquid crystalline order (Figure 4B, right, Figure 4A). This implies that by the illumination of a sample one can induce the actuation of an LCN isothermally, with the maximum contraction observed for $cis - T_{NI} < T < trans - T_{NI}$ (since the larger the change in the order parameter, the larger the contraction). In addition, the decrease in the photosensitive molecules' lengths occurring upon the conformation change also contributes to the actuation. The LCN restores its initial shape after switching the light off due to the spontaneous thermal back-isomerization of the photosensitive molecules. If no measures to remove unnecessary wavelengths are taken, the sample heating under light can also contribute to the actuation process.

This mechanism of actuation allows one to use light of a wide range of wavelengths as an external stimulus, namely UV, VIS and NIR light. Azobenzene derivatives normally need UV light to transform from the trans- to the cis-form (Figure 4C) (Pang et al., 2019). This part of the EM spectrum can be used for applications where actuators are not supposed to interact with living beings.
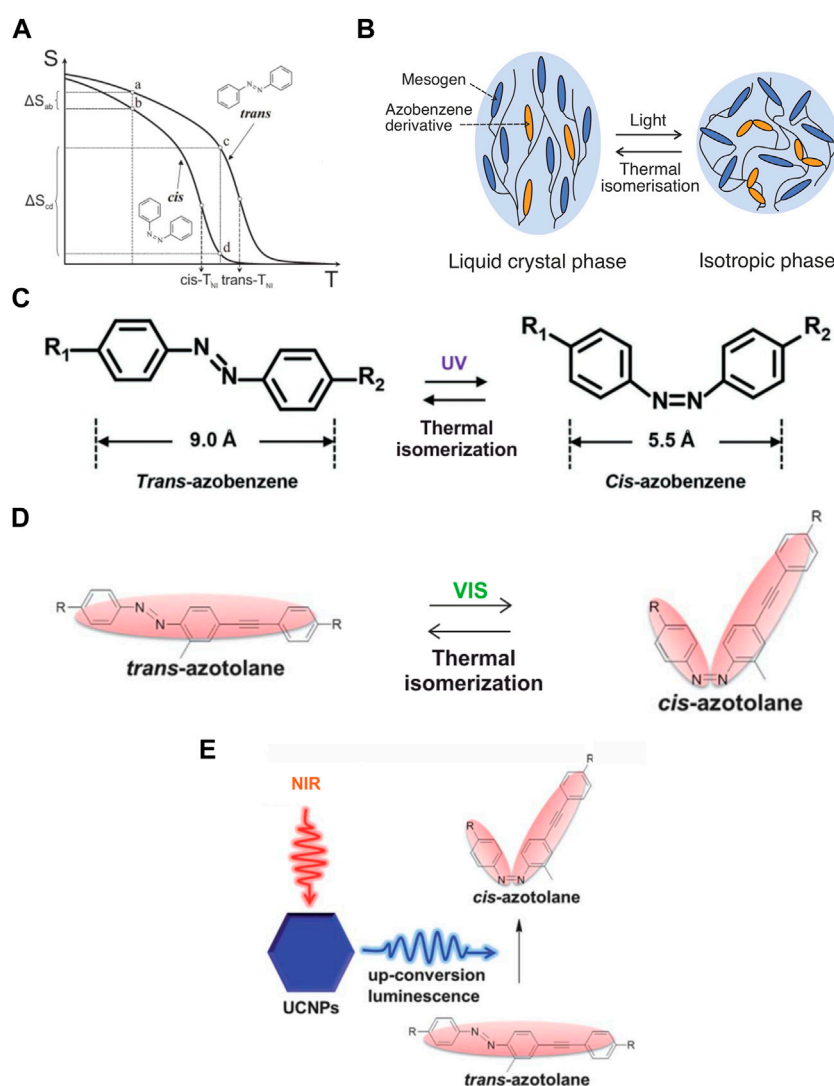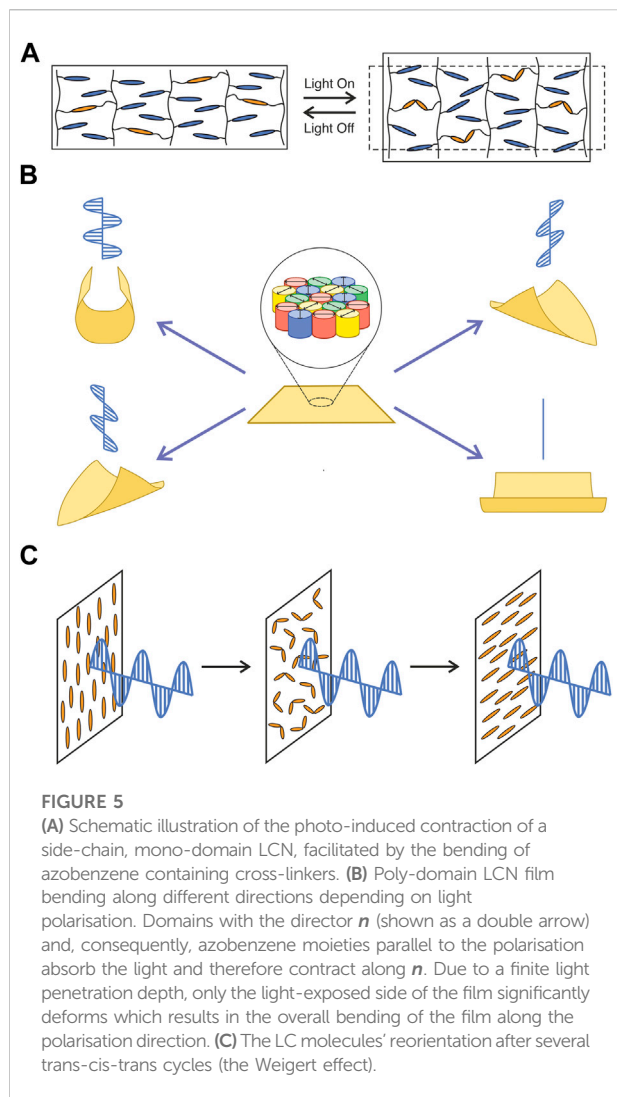
FIGURE 4
(A) The temperature dependence of the order parameter S for a mono-domain LCN with azobenzene moieties in the trans and cis-form. Reprinted with permission from Sánchez-Ferrer et al. (2011). Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. **(B)** Schematic illustration of the photo-induced deformation of an LCN's small element. **(C)** Azobenzene derivative in the trans- and cis-forms. Reprinted with permission from Pang et al. (2019). Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. **(D)** Azotolane derivative in the trans- and cis-form. Reprinted with permission from Wu et al. (2011). Copyright 2011 American Chemical Society. **(E)** Schematic illustration of the NIR to VIS or UV light conversion by upconversion nanophosphors (UCNPs). Reprinted with permission from Wu et al. (2011). Copyright 2011 American Chemical Society.

However, if bio-medical applications are concerned, it is desirable to use VIS or NIR light as those are not harmful for biological substances. To shift the absorbance peak towards visible wavelengths, the use of azotolane instead of azobenzene derivatives was suggested (Figure 4D) (Yin et al., 2009; Zhao and Yu, 2014). NIR light can be used as an external stimulus if upconversion nanophosphors are incorporated into an LCN (Wu et al., 2011). An upconversion nanophosphor absorbs several NIR photons and then emits a single photon of a shorter wavelength in the UV or VIS range (Figure 4E), in a process known as upconversion luminescence. It is also possible to create a UV-VIS-NIR responsive actuator by incorporating both azobenzenes (for UV light-triggered photo-induced actuation) and graphene oxide (for VIS and NIR light-triggered photo-thermally induced actuation) (Cheng et al., 2015).

Azobenzene moieties can help to enhance mechanical properties if they are part of cross-linkers: they fold on light illumination and in this way pack polymer chains closer to each other, facilitating a contraction in the case of side-chain LCNs with the mutually orthogonal orientation of polymer chains and the director (Figure 5A) (Sánchez-Ferrer et al., 2011). Interesting concepts of actuation emerge if attention is paid to the incident

FIGURE 5
(A) Schematic illustration of the photo-induced contraction of a side-chain, mono-domain LCN, facilitated by the bending of azobenzene containing cross-linkers. **(B)** Poly-domain LCN film bending along different directions depending on light polarisation. Domains with the director *n* (shown as a double arrow) and, consequently, azobenzene moieties parallel to the polarisation absorb the light and therefore contract along *n*. Due to a finite light penetration depth, only the light-exposed side of the film significantly deforms which results in the overall bending of the film along the polarisation direction. **(C)** The LC molecules' reorientation after several trans-cis-trans cycles (the Weigert effect).

light polarization. For example, Yu et al. (2003) showed that polydomain LCNs can also be effectively used for actuating devices. The authors irradiated a poly-domain LCN film with polarised light and observed a film bending along the polarisation direction (Figure 5B). The reason for such behaviour is that the light absorption efficiency of azobenzene derivatives is higher for light polarised along the $N = N$ double bond. The majority of azobenzene moieties were incorporated into LC units and so were aligned with them. Therefore the light was effectively absorbed only by domains with the director orientation parallel to the polarisation direction, and only such domains contracted. Since the light penetration depth is finite, only the light-exposed side of the film was significantly deformed which resulted in the overall bending of the sample. The Weigert effect, in which after several trans-cis-trans cycles azobenzene molecules become oriented perpendicular to the light polarisation, can be used to change the LC units' orientation and in this way trigger shape deformations of LC-polymer

systems (Figure 5) (Lv et al., 2016; Pang et al., 2019). In addition, switching-off response times can be sped up by accelerating the cis-trans transition with VIS light (Yu et al., 2003; Yin et al., 2009). Moreover, the benefits mentioned for the photo-thermally induced actuation are relevant for this case as well.

Disadvantages of such a mechanism include the limited number of suitable photosensitive molecules, the degradation of actuators caused by side reactions and photo-degradation, and sample bending due to the finite light penetration depth (Dong and Zhao, 2018).

Finally, it must be noted that the discussed photo-induced decrease in the liquid crystalline order and Weigert effect are well observed in liquid crystal elastomers but not in liquid crystal thermosets which are cross-linked too densely. Light-triggered actuation of the latter is mostly related to the change in photosensitive molecules length upon the transition from the rod-like to the bent state (White, 2018).

5 Chemically induced actuation

In the case of a special chemical design, LCNs can be forced to deform in response to the chemical composition of the environment. There are several concepts of creating such LCN systems. Let us consider several of them in somewhat more detail.

5.1 LCNs with breakable mesogenic units

One of the concepts was suggested by Harris et al., 2007, Harris et al. (2005) and is based on LCNs in which the role of the mesogens is played by the polymer side-chains, paired in rod-like clusters *via* secondary bonds (Figure 6A, top). The bonds should be able to reversibly break or form in response to a certain chemical stimulus resulting in the change of the liquid crystalline order. The latter is expected to cause either LCN contraction along the director and its elongation perpendicular to it in case of decreasing order (bonds being broken) or the opposite behaviour in case of increasing order (bonds being formed).

With this idea in mind, the authors created a pH responsive LCN. The LCN's polymer side-chains were caped with carboxylic acid units and paired in rod-like clusters *via* hydrogen bonds between the units. It was shown that the bonds could be effectively broken by LCN exposure to a high pH potassium hydroxide (KOH) solution which led to LCN actuation (Harris et al., 2005). In a later study on the same system (Harris et al., 2007), the authors demonstrated that instead of the expected contraction, an elongation along the director was observed, but the deformation was much smaller than the elongation in the plane orthogonal to the director and was attributed to network swelling in the KOH solution.
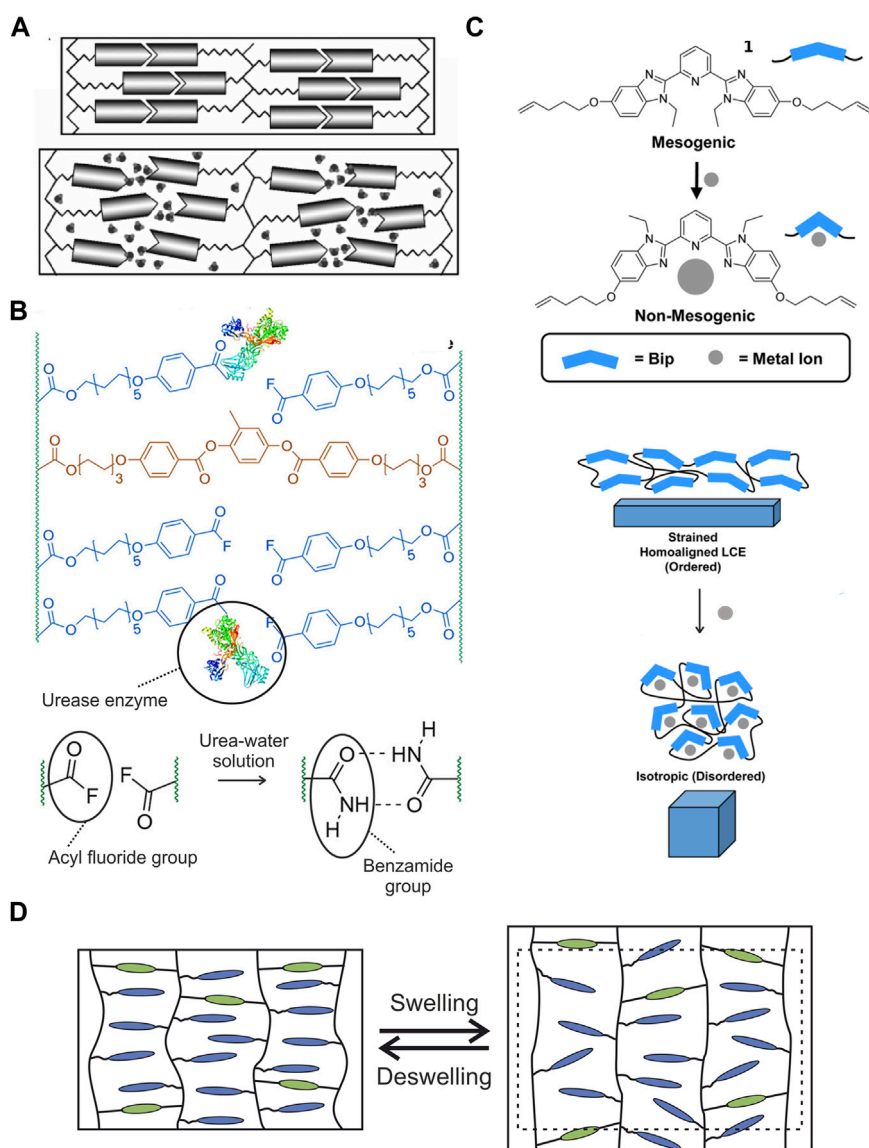
FIGURE 6
(A) Mono-domain LCN, in which the role of mesogens is played by side-chains, paired in rod-like clusters by secondary bonds (top), and the shape change of the LCN caused by the breaking of the bonds after a certain change in the chemical composition of the environment (bottom). Reprinted with permission from Harris et al. (2005). Copyright 2005 American Chemical Society **(B)** The architecture of an LCN with the immobilized ureazse enzyme (top) and the scheme of the chemical reaction, leading to the creation of secondary bonds between side-chains (bottom). Reprinted with permission from Velasco Abadia et al. (2021). Copyright 2021 American Chemical Society. **(C)** Conformational change of a Bip-based derivative caused by its interaction with a metal ion (top) and the corresponding deformation of a mono-domain LCN. Reprinted with permission from Michal et al. (2015). Copyright 2015 American Chemical Society. **(D)** Schematic illustration of LCN actuation through the anisotropic swelling mechanism shown for a side-chain, mono-domain LCN.

Other chemical stimuli can also be used to trigger LCN actuation. For example, Velasco Abadia et al. (2021) created an LCN responsive to urea. To achieve this, the authors immobilized the urease enzyme at the ends of some of the side-chains as it is shown in Figure 6B, top. In a water-urea solution, the enzyme catalysed a reaction between urea and water, which yielded ammonia as one of the products. The ammonia reacted with the acyl fluoride groups on the side-chains' ends (which were not connected with the urease),

generating benzamide groups (Figure 6B, bottom). In turn, the benzamide groups formed hydrogen bonds with each other, thus forming rod-like clusters and consequently increasing the liquid crystalline order. The latter resulted in LCN elongation along the director and contraction perpendicular to it (Velasco Abadia et al., 2021). The idea of using urease to trigger LCN actuation was further investigated and developed by the group in their later study (Abadia et al., 2022).

The discussed mechanism utilizing breakable mesogenic units can be tailored to other chemical reactions, giving a unique opportunity to broaden the range of chemical stimuli. The two studies by Velasco Abadia et al. (2021) and Abadia et al. (2022) made a significant step forward in this direction since there is the rich variety of enzymes in nature.

5.2 LCNs with mesogenic units capable of conformational changes

The second actuation concept is generally similar to the previous one, but in this case the change in liquid crystalline order results from the conformational change of mesogenic units in response to a chemical stimulus. A good illustration of this concept is the study by Michal et al. (2015) in which the authors prepared an LCN with mesogenic units sensitive to the presence of metal ions. In this study, a polymer network contained Bip-based derivatives as monomers (Bip: 2,6-bis (ben-zimidazolyl)-4-pyridine). In their usual configuration, the Bip-based derivatives are rod-like and tend to form an LC phase, whereas in the presence of metal ions, due to the ligand nature of Bip, they form a complex with the ions, and consequently bend, losing their liquid crystalline nature (Figure 6C, top). Therefore, when the LCN was exposed to a Fe^{2+} ion solution, the decrease in LC order occurred, resulting in LCN actuation (Figure 6C, bottom). In general, different sources of metal ions such as transition metal and lanthanide salts can serve as actuation triggers (Michal et al., 2015). One can also expect that it is possible to replace Bip with other ligands.

5.3 LCN actuation through anisotropic swelling

This actuation concept exploits the ability of polymer networks to swell in response to a chemical stimulus and the ability of LC units to influence the alignment of polymer chains in a network. Indeed, in a mono-domain LCN, the coupling between the alignment of the LC units and polymer main-chains leads to the macroscopically anisotropic architecture of the network. Due to this fact, one can expect that the swelling process in LCNs should occur anisotropically as well, with network elongation being more pronounced in some particular direction (which would depend on the way the LC units are oriented relative to the main-chains), i.e., anisotropic LCN actuation should be observed (Figure 6D).

There are several mechanisms of polymer network swelling. One of them is based on the swelling of polyelectrolyte networks due to their ionization and can be illustrated on the same study by Harris et al. (2007), Harris et al. (2005) discussed earlier. In this work, the side-chain LCN exposure to a high pH KOH solution not only caused a decrease in LC order but also converted the carboxylic acid units into dissociable carboxylic acid salts of potassium and in this way made the network capable of ionization, i.e., transformed it into a polyelectrolyte. Therefore, in the presence of water, the salt units dissociated into ions, and the free K^+ ions dispersed in water within the network causing an osmotic pressure which led the network to expand. The KOH treatment partly preserved the liquid crystalline order (though this decreased due to the hydrogen bond breakage), and hence the network swelling occurred anisotropically, showing the largest elongation in the plane orthogonal to the director (Harris et al., 2005). The more detailed study of the actuation process of this system was done in the latter study (Harris et al., 2007) by the same group.

Boothby et al. (2017) exploited another swelling mechanism, which was based on LCN exposure to good solvents. By definition, a solvent is good for a given polymer if interactions between the polymer and the solvent are energetically beneficial. Due to this fact, polymer chains tend to expand in a good solvent in order to increase the amount of interaction. Therefore, an LCN exposed to a good solvent should swell. The authors demonstrated that their side-chain LCN indeed swelled in such organic solvents as tetrahydrofuran, acetone, dimethylformamide, and chloroform. Notably, the LCN did not expand in all directions as it was expected, yet with different efficiency. Instead, along the director a contraction was observed. It was hypothesized that the swelling related expansion in this direction was suppressed by the contraction due to the LC order decrease caused by the dilution of LC units which resulted from the increase in the sample volume.

In general, depending on the chemical design of a LCN and the chosen swelling mechanism, different solvents can be used as triggers, including water (Harris et al., 2005; de Haan et al., 2014; Liu Y et al., 2017), tetrahydrofuran, acetone, dimethylformamide, and chloroform (Boothby et al., 2017) as discussed above. Notably, the swelling of an LCN in a low molecular weight liquid crystals (LMWLCs) is a particularly interesting direction of research due to a rich variety of phenomena related to the orientational order of LMWLC in an LCN matrix (Yusuf et al., 2004b; 2004a; Matsuyama and Kushibe, 2010).

In general, chemically responsive LCNs have the advantage of a large variety of chemicals that can be used as triggers. At the same time, additional consideration should be given to the way of restoring the initial sample shape since this depends on the chemical reactions employed. The discussed actuation mechanisms can be used in drug technologies and various sensors (e.g., pH, humidity, metal ion sensors), while it seems to be difficult to use them in robotics.

6 Electrically induced actuation

Liquid crystals are often highly responsive to the electric fields, and this property gives an opportunity to use the latter to
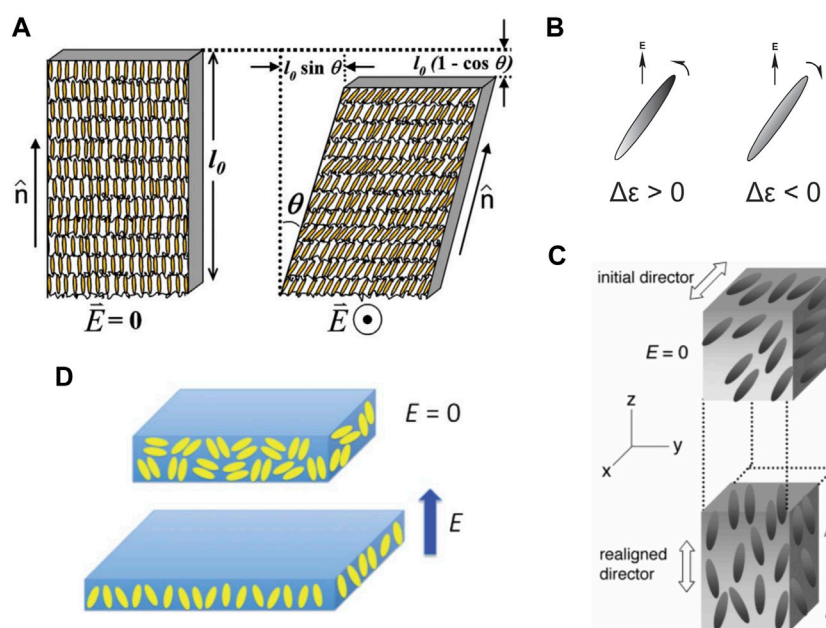
FIGURE 7
(A) Shematic illustration of the electroclinik effect in a SmA* LCN. Reprinted with permission from Spillmann et al. (2007b). Copyright 2007 AIP Publishing. **(B)** The LC molecules' rotation in the electric field in case of positive and negative dielectric anisotropy. Reprinted from Huang et al. (2003). Copyright 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Deformation of a mono-domain (Urayama et al., 2006) **(C)** and poly-domain (Okamoto et al., 2011) **(D)** LCNs caused by the LC units' realignment in the electric field. **(C)** Reprinted with permission from Urayama et al. (2006). Copyright 2006 American Chemical Society. **(D)** Reprinted with permission from Okamoto et al. (2011). Copyright 2006 Royal Society of Chemistry.

trigger LCN actuation. Let us consider the two main mechanisms of electrically induced actuation that have been suggested to date.

6.1 Electroclinic effect in chiral smectic A

The electroclinic effect, first demonstrated by Garoff and Meyer (Garoff and Meyer, 1979; Garoff and Meyer, 1977), is a unique phenomena observed in chiral smectic phases and is most often described for the smectic A* (SmA^*) phase (Figure 7A, left). If an electric field is applied perpendicular to the director the LC molecules tilt in a plane orthogonal to the field, forming an induced chiral smectic C* (SmC^*) state (Figure 7A, right). The effect is highly temperature dependent and most pronounced at the transition temperature from SmA* to SmC*. It can be observed on both sides of the transition, although often obscured by ferroelectric switching in SmC*. One can expect that the electroclinic effect in LCNs exhibiting the SmA^* phase should result in a reversible two-dimensional deformation of the network: along the layer normal and along the direction parallel to the smectic layers and orthogonal to the applied electric field direction (Figure 7A). For LCNs It was first suggested and shown in the study by Lehmann et al. (2001).

The magnitude and direction of deformations (contraction/elongation) for such systems are independent of the electric filed polarity (Köhler et al., 2005; Spillmann et al., 2007b). The largest mechanical response to the electric field is usually observed at temperatures in the vicinity of the transition between SmA^* and SmC^* phases for an uncross-linked mixture used to prepare an LCN (Lehmann et al., 2001; Köhler et al., 2005). From the dependence of deformation magnitudes on the induced tilt angle θ between the director and the layer normal, one can derive their dependence on the applied electric field E. Assuming a linear dependence of the induced tilt angle on the electric field, $\theta = \alpha E$, where α is the electroclinic coefficient, and applying the small angle approximation to an equation for the deformation along the layer normal,

$$\frac{\Delta l}{l_0} = -(1 - \cos\theta)$$

(see Figure 7A), where $\frac{\Delta l}{l_0}$ is the strain, one obtains,

$$\frac{\Delta l}{l_0} = -\frac{\theta^2}{2} = -\frac{\alpha^2 E^2}{2} = -aE^2$$

Since this dependence is quadratic, this deformation is of electrostrictive nature (Damjanovic and Newnham, 1992),
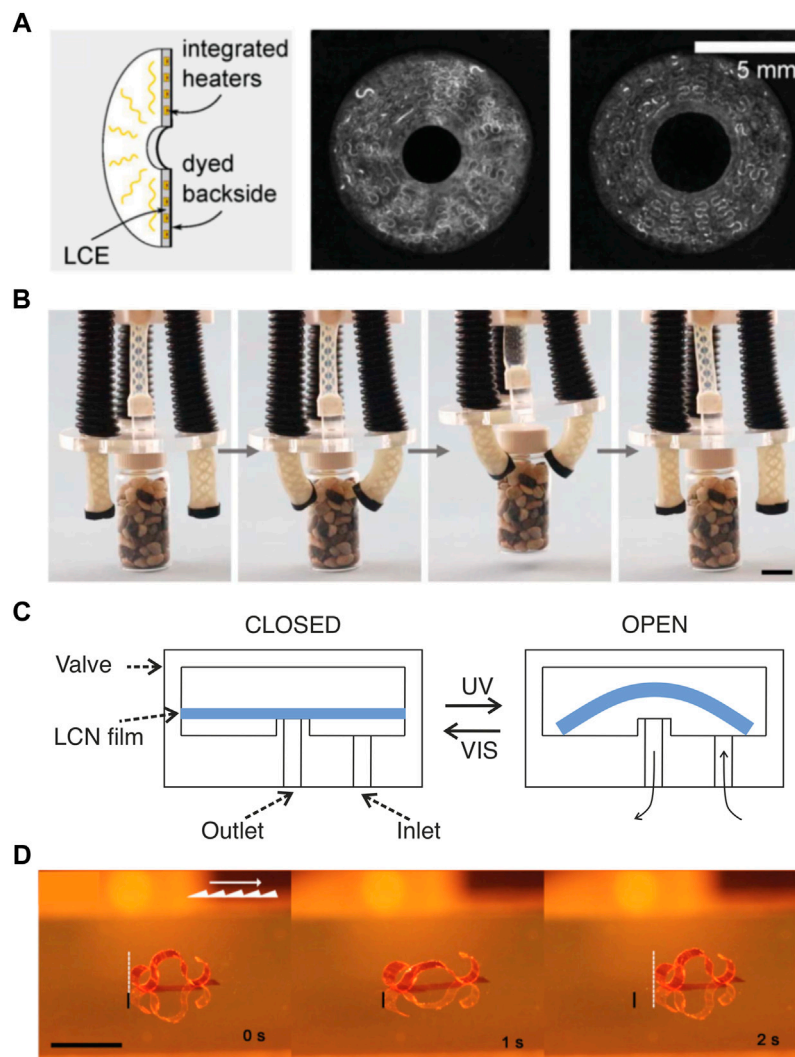
FIGURE 8
(A) Compact electrically controlled aperture, made of an LCN with conductive wires, for a phone camera. Reprinted with permission from Schuhladen et al. (2014). Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. **(B)** Griper, made of an LCN with conductive wires. Reprinted with permission from He et al. (2019b). Copyright 2019 AAAS. **(C)** Schematic illustration of a photo-controlled valve with an LCN membrane suggested in Chen et al. (2011). **(D)** Caterpillar-like walker powered by temporally modulated light. Reprinted with permission from Zeng et al. (2018). Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

with a being the electrostriction coefficient. Using the same assumptions for the second type of deformation, one obtains

$$\frac{\Delta l}{l_0} = \sin\theta = \theta = \alpha E$$

which corresponds to the piezoelectric effect (Damjanovic and Newnham, 1992). However, only the electrostrictive effect was confirmed in experiments (Lehmann et al., 2001; Köhler et al., 2005; Spillmann et al., 2007b), while for the second type of deformation the derived dependence does not hold (Spillmann et al., 2007b).

An advantage of this mechanism is the possibility of the remote control. Moreover, an electrostriction coefficient of up to $0.001\,m^2MV^{-2}$ is achievable (Köhler et al., 2005), which allows to relate such LCN systems to electrosctrictive materials with some of the largest electrostriction coefficients (Lehmann et al., 2001). However, attention should be paid to the design of such actuators since any external stress imposed on LCNs can suppress the electrically induced deformations (Köhler et al., 2005).

It should be noted that the same deformations can be induced by the transition between SmA^* and SmC^* phase through the heating/cooling of a sample (Hiraoka et al., 2005).

6.2 Realignment of LC units by the electric field

It is well known that due to their non-zero dielectric anisotropy, $\Delta\varepsilon$, LC molecules tend to reorient in the presence of the electric field: if $\Delta\varepsilon$ is positive, then LC molecules rotate toward the electric field; if $\Delta\varepsilon$ is negative, the molecules rotate away from it (Figure 7B) (Chandrasekhar, 1992; de Gennes and Prost, 1995; Collings and Goodby, 2019). This characteristic behaviour can be used to trigger the actuation of LCNs. The most common and simple geometry of experiments is a homogeneous film of a sidechain LCN, swollen in a LMWLC and subjected to an electric field perpendicular to its plane (Zentel, 1986; Urayama et al., 2006; Urayama et al., 2005a). In this case, for mesogenic units with $\Delta\varepsilon > 0$, a film elongates along the electric field and contracts along the initial director (Figure 7C) with reversible deformations. Similar to the Freedericksz transition observed in LMWLC cells, the LC units' reorientation, leading to the deformations, takes place only when E is larger than some threshold field. An interesting approach to enhance the actuation performance is using poly-domain LCN films instead of mono-domain samples (Figure 7D). It was shown that the threshold E is lower in such systems, while deformations are larger. However, the contraction of a sample along E instead of the expected elongation was observed, indicating that the underlying deformation mechanism is different in this case. To our knowledge an explanation of the process is not yet provided (Okamoto et al., 2011).

The discussed mechanism enables the remotely controlled actuation. However, as in the previous case, the electrically induced deformations are partially or completely suppressed in constrained films. (Qin and Yu 2017). Suspending films in silicon oil (Urayama et al., 2006; 2005a) or LMWLC (Zentel, 1986) is often used to prevent this effect. A theoretical consideration of actuation in constrained and unconstrained geometries can be found in (Terentjev et al., 1994).

Other deformation effects can be achieved if one changes an LCN architecture or the sign of LC units' dielectric anisotropy in the network and the surrounding solution (Huang et al., 2003; Urayama et al., 2005b).

7 Discussion

In this review, we provided an overview of the main LCN actuation mechanisms. The most popular and well-studied are the mechanisms of actuation based on thermal changes, which cause a change of the order parameter and therefore a change of the length of the LCN. This can be achieved by a range of different methods, for example heating through thermal conduction, photo-induced heating, electrically induced heating or magnetically induced heating. In any case it is preferable and simple from an applicational point of view to choose a method that is contactless, whenever possible, although this does obviously depend on the specific application and its performance requirements. For the latter reason, also the photo-induced actuation has been developed, which acts on the basis of trans-cis isomerisation of suitable mesogenic units, nearly exclusively containing azo-groups. Some actuators, mainly in the field of sensors, are required to react to chemical changes in the environment. In such actuators, mesogenic units used are often based on breakable bonds or are capable of conformational changes. Anisotropic swelling can also be employed to produce a chemoresponsive actuator. At last, a popular mechanism for actuation of liquid crystal networks is that *via* electrically induced shape- and order parameter changes. Here the electroclinic effect, which is electrostrictive in nature, is exploited, leading to a polarity independent, linear shape change of the LCN with applied electric field. Other electrical mechanisms are based on the realignment of the mesogens. To keep this review introductory, we considered only the basic principles of the described actuation mechanisms. However, theoretical and computer models, which quantitively describe the relation between stimulus and/or material parameters and the induced deformations, are being developed to facilitate the development of programable LCN devices. The recent overview of the results in this research direction can be found in (Soltani et al., 2021).

In order to provide a general idea (but by no means a comprehensive characterisation) of LCN mechanical performance, we have collected relative shape changes, actuation times, and exerted stresses from several discussed articles in Supplementary Table S1. From the table follows that the achieved length changes are of the order of several tens of percent (~30%–50%) for average actuation time of the order of several seconds, up to minutes. Only the electrically induced actuation can occur at faster times of several milliseconds. It must be noted that in certain cases LCNs can change their dimensions by several hundred percent (Ahir et al., 2006). Stresses observed in the discussed articles range from tens to hundreds kPa although values of up to several GPa can also be achieved (White, 2018). In comparison to other types of soft actuators, which include electroactive, magnetoactive, ferroelectric, and shape memory polymers, hydrogels, shape memory alloys, and others, LCNs are generally slower but, at the same time, show large deformations. In terms of exerted stresses, these materials are comparable to other polymer-based soft actuators. Importantly, since the mechanical characteristics of an LCN actuator depend on its chemical and physical design, the proper tuning of the latter can often help to attain desired

performance values. In addition to mechanical characteristics, such factors as production feasibility, the reversibility of deformations, material lifetime, and others should be considered when choosing a soft actuator type. A comprehensive comparison of different soft actuators in terms of various aspects can be found in (Apsite et al., 2022; Hao et al., 2022).

Today, LCN fabrication technologies and the understanding of the involved processes appear to have matured to a point suitable for the design of actual real devices. All actuation mechanisms have different advantages and disadvantages, and the prioritisation of one over the other needs to be based on the device requirements. A large range of different concepts of LCN actuators applications has already been suggested, e.g., in the fields of 1) waste-energy harvesting (Wei et al., 2018; Han et al., 2020), 2) microfluidics [pumps (Chen et al., 2010), valves (Chen et al., 2011), smart channels (Lv et al., 2016)], 3) smart surfaces (Nagai et al., 2016; Liu D et al., 2017; Ryabchun et al., 2021), 4) biomimetic technologies (Yang and Zhao, 2018; Zeng et al., 2018), 5) optical devices (Schuhladen et al., 2014; López-Valdeolivas et al., 2018), 6) soft robotics, and 7) medicine [drug technologies, artificial muscles (Thomsen et al., 2001; Ambrogi et al., 2005; Dong and Zhao, 2018)] (Figure 8). The results in this directions are summarised by a number of review articles (Jiang et al., 2013; Ula et al., 2018; Shang et al., 2019; Zhu et al., 2021). Investigations, aiming on more specific goals and supported by industry, could help to accelerate the development of technologies based on LCN actuators. In any case, this field of research is promising in materials design and will provide results and applications which will be useful in the future.

Author contributions

AG wrote the first draft of the review manuscript, which was critically revised by ID. The final manuscript was approved by all authors.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/frsfm.2022.1052037/full#supplementary-material

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