

Review

# Reversible Crosslinking of LC-Materials by Gel-Formation

Rudolf Zentel 

Department of Chemistry, Johannes Gutenberg University of Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany; zentel@uni-mainz.de; Tel.: +49-6131-39-20361

**Abstract:** The topic of this review is the physical gelling of liquid crystalline (LC) phases. It allows the combination of order and mobility of the LC-phase with macroscopic stability, which makes it a soft material. Thus, the gelled LCs acquire properties of LC-elastomers without the need for complicated chemistry to allow polymerization and crosslinking. But, instead, an LC-material (either a pure compound or a mixture) can be mixed with a few percent of a gel-forming agent, which self-assembles into long fibers that span the volume of the gel and make it a soft-solid. The use of azo-containing gel-forming agents thereby allows us to make gelation not only thermo-responsive, but also photo-responsive (trans-cis isomerization). This review discusses the micro-morphology of the gelled LCs and their influence on the mechanical properties and the switching in external electric fields. In addition, the potential of reversibility is discussed, which is not only interesting for recycling purposes, but also offers a route to inscribe a complex director pattern into the gelled liquid crystal.

**Keywords:** LC-materials; gelling; LC-elastomers; switching in E-fields

## 1. Introduction

Gelation is a well-known phenomenon [1–4], by which a liquid-like compound is transferred into a soft solid by a small amount of a gelling agent, which spans the volume and thereby creates the possibility to withstand some mechanical forces (i.e. to achieve some elastic mechanical modulus). A typical example for this is the self-assembly of small molecules [1] into 1D (one-dimensional) fibers in a liquid solvent. Thereafter, these fibers can pick up the mechanical load to solidify the sample macroscopically, whereas the majority of the compound is still in a liquid state. Gelation is thereby often reversible and can be reversed, e.g., by a temperature increase, if the 3D aggregate can dissolve, disentangle, etc., again.

Gelation is, however, not only possible in classical (isotropic) liquids. It can also be conducted in liquid crystalline phases (see Figure 1), whereby the liquid crystalline phase is transferred into a soft solid with an elastic modulus, while the local order and mobility of the LC-phase are retained [5–10]. These gelled liquid crystalline materials were introduced by Kato et al. and Zentel et al. Their structure, their properties, and their potential will be the topic of this review.

Liquid crystalline (LC) phases—often also called mesophases—are thermodynamically stable phases existing in a temperature interval between typical crystals (as solids) and the typical isotropic liquid [11]. These phases combine, therefore, some (long-range) order (they are birefringent) with mobility. Their internal structure is schematically presented in Figure 1. Nematic phases are typically the high-temperature phase and possess a low viscosity, while the smectic phases are more viscous.



**Citation:** Zentel, R. Reversible Crosslinking of LC-Materials by Gel-Formation. *Crystals* **2024**, *14*, 466. <https://doi.org/10.3390/cryst14050466>

Academic Editor: Pedro De Almeida

Received: 17 April 2024

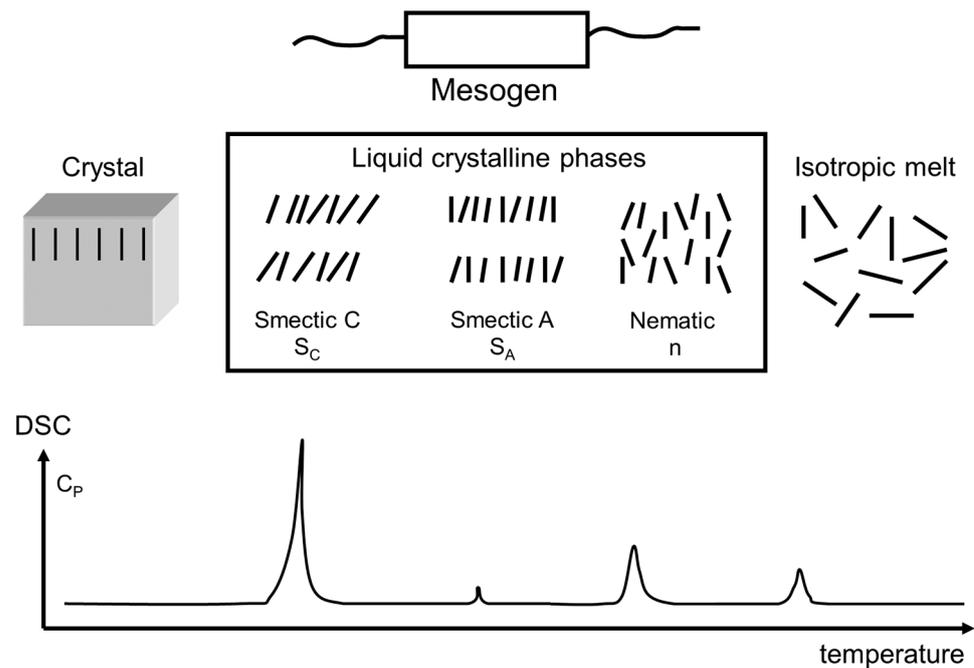
Revised: 11 May 2024

Accepted: 13 May 2024

Published: 16 May 2024



**Copyright:** © 2024 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).



**Figure 1.** Schematic representation of various thermotropic LC-phases, which are formed by form-anisotropic constituents (the so-called “mesogens”) and exist in a temperature interval between the crystalline phase and the isotropic liquid. They are separated from each other and the other phases by phase transitions, which are usually accompanied by a transition enthalpy. Thus, the phase transitions can be detected by DSC-measurements (below). Picture modified and redrawn from ref. [11] with allowance of Wiley-VCH.

## 2. Specialties during Gelling in LC-Phases

While it is obvious that the formation of long 1D fibers in isotropic liquids and in an LC (liquid crystalline)-phase will change their mechanical (elastic) properties, there is an additional effect in LC-phases, which is due to the order in the LC-phase and its interaction with surfaces (the LC-director will preferably orient parallel or perpendicular to the surface [12]). Now, during gelation a large amount of new surface will be created at the fiber structure formed and this surface and its influence on the LC-director field will add to gelation. And this effect is already valid for sphere-like nanoparticles dispersed in an LC-Phase [12].

In general, the presence of lots of nanoparticles leads to a very complex pattern of the LC-director (an LC-director pattern very different from a monodomain) and it disturbs the LC-order of the mesogens [13–15] (this may be different for lyotropic LC-phases formed from anisotropic nanoparticles themselves [16]). And this increases the energy of the corresponding LC-phase. Thus, the LC-phase tries to exclude the nanoparticles. As a consequence, a phase separation into the pure LC-phase and small mixed phases at the interface occurs [12], which is very rich in nanoparticles. This two-phase structure leads to an increase in the viscosity. In addition, the director configuration around nanoparticles leads to long-range interactions between them, which have an additional effect on the viscosity.

The accumulation of nanoparticles from the pure LC-phase is especially prominent in smectic phases, where they have been detected [13,17,18] to concentrate at defect sides within the smectic texture.

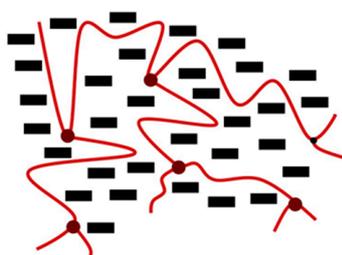
Altogether, this additional effect can already lead to a gelation of nematic and cholesteric phases just by adding small amounts of spherical colloids [12,19,20]. The effects of long fibers are much more dramatic. Therefore, generally, the incorporation of nanoparticles into LC-phases offers a method for their gelation [5,21] and will lead to the formation of soft materials with LC-phases, which are similar to LC-elastomers [22–27]. And this gelation

can be made reversible if the formation of the nanoparticles can be made reversible (by temperature change or irradiation).

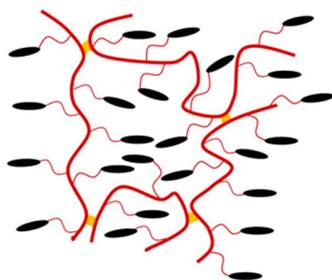
### 3. General Concepts for the Preparation of LC-Elastomers

Elastomers—in general—are defined by their macroscopic mechanical properties, i.e., they are materials which act macroscopically as soft solids; this means that they can withstand stress without a macroscopic flow. But at the same time, they can be deformed quickly and easily to a larger extent. And this requires a sufficient local, liquid-like mobility. To combine the properties of liquids and solids in one material, elastomers are—in some way—composed of two subsystems (see Figure 2a). There has to be a structure, which expands into the macroscopic volume, to achieve solid-like properties like an elastic modulus and a liquid-like component to contribute the local mobility. In typical elastomers, the liquid-like component is attributed by liquid-like polymer chains or a typical isotropic liquid, with which the network is swollen.

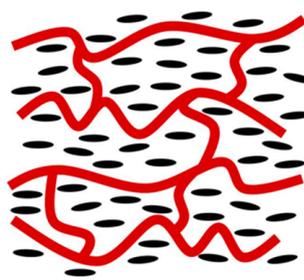
#### (a) Liquid crystals and networks



#### (b) LC-Elastomers



#### (c) Fiber stabilized liquid crystals



**Figure 2.** Schematic presentation of the generation of LC-materials, in which liquid crystalline order and mobility are coupled to a macroscopic solid-like behavior. (a) Very general idea to couple a macroscopically crosslinked network (red) and a liquid crystal (black), just by putting them in the same place. (b) LC-elastomers, in which the mesogens (black) are linked to liquid crystalline polymers (red), which are then covalently crosslinked to create a macroscopic network. (c) Nanophase separated systems, in which a three-dimensional percolated fiber structure (red, the fibers are thicker than the mesogens) is filled with a low molar mass liquid crystal (black). This situation is realized in gelled liquid crystals.

In this picture, to obtain an LC-elastomer the isotropic liquid has to be exchanged with a liquid crystalline material (see Figure 1), in which the mesogens self-organize in liquid crystalline phases at given temperature intervals [22–25]. In the typical LC-elastomers this is achieved by linking the mesogens covalently to the polymer network, which expands into the volume and adds elasticity (see Figure 2b) [22,24,28,29]. However, the properties of an LC-elastomer can also be obtained by filling a liquid crystalline phase with long nano-sized fibers, which percolate to achieve the macroscopic stability (see Figure 2c). These systems will be described here.

Now, soft elastic materials with an LC-phase (usually LC-elastomers) possess many properties, which make them very special and fascinating materials [11,22–27,29–31]. They stem from the interplay [11] between the liquid crystalline director and the deformation of the network (change in its shape). Thus, in such systems it is possible to change the director pattern by a mechanical deformation and—vice versa—to change the shape of the sample by changing the director pattern (see Scheme 1). Most fascinating (and mostly studied at present) are their properties as stimuli-responsive mechanical actuators [26,27,31–33], which change their size and shape during the variation in temperature or during illumination. But, in combination with the switching of liquid crystalline materials (e.g., in electric fields, in LC-displays) they also offer the possibility to stabilize a director pattern against unwanted variations or to facilitate the return of the director field to the ground state, after the electric field is removed [14,34,35]. Important for these applications is therefore the strength of the coupling between the orientation of the mesogenic groups (described by the LC-director) and the macroscopic mechanical properties of the LC-elastomer, which depend on the macroscopic network. To prepare good mechanical actuators, which change their size strongly at the transition between the LC and the isotropic phase and are able to supply mechanical work, systems with a strong coupling are desired [11,22,31]. For systems which shall be applied during switching in electric fields and where it is the goal only to stabilize one state, a weak coupling is desired [14,22,34–36].

For LC-elastomers with chiral LC-phases, like cholesteric and chiral smectic C\* phases, additional fascinating properties emerge [11] (see Scheme 1). Cholesteric phases show selective reflection of light of a special wavelength. Here, it becomes possible to change the wavelength of the reflected light by mechanical deformations [37] or to untwist the chiral superstructure of the cholesteric phase [11]. This could be used to tune mirrorless lasing in cholesteric elastomers [37].

Chiral smectic C\* phases are fascinating because they possess ferroelectric properties [22,38,39]. This makes their incorporation into LC-elastomers very interesting because the coupling between the LC-director and the macroscopic network transforms a deformation of such LC-elastomers into strong piezo effects [22,38,39]. On the other hand, the application of electric fields leads directly to size variations of the elastomers [22]. In this context, a good coupling to change the director field by a mechanical deformation is desirable [11,35]. During studies on cholesteric LC-elastomers, it was observed that they also show piezo effects [38,40]. The fascinating materials effects (Scheme 1) mentioned above have been known for many years. Recent work focuses on their practical applications (see e.g., ref. [31,41]).

### **Coupling of the macroscopic elasticity of a network and the anisotropic order of the LC-phase**

#### Limit of strong coupling:

- Change of the shape of the sample while varying the LC-order => mechanical actuators as response to temperature variation or illumination
- Change of the director pattern by deformation of the sample

#### Limit of weak coupling :

- Stabilization of the director pattern, while electrical switching is still possible

#### Combining mechanical orientability with more special LC-properties:

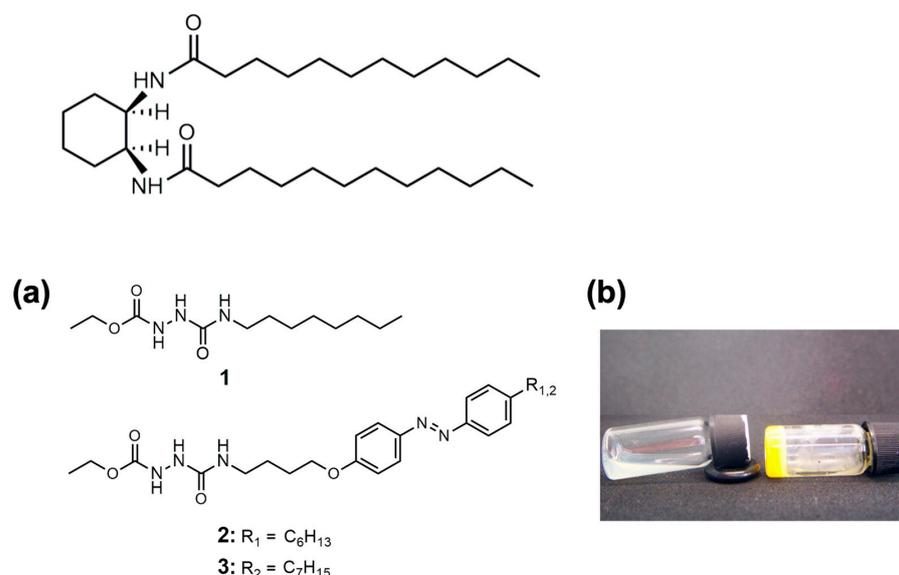
- Cholesteric phases => variation of the optical reflection
- Chiral smectic C\* phases => piezo-effects

**Scheme 1.** Materials properties resulting from the coupling of elasticity and LC-phases. Refs. for strong coupling [11,22,23,25,27,29,30,32,33]; refs. for weak coupling [34]; cholesterics [37]; chiral smectic C\* [36,39].

#### 4. Gelation to Prepare LC-Elastomers

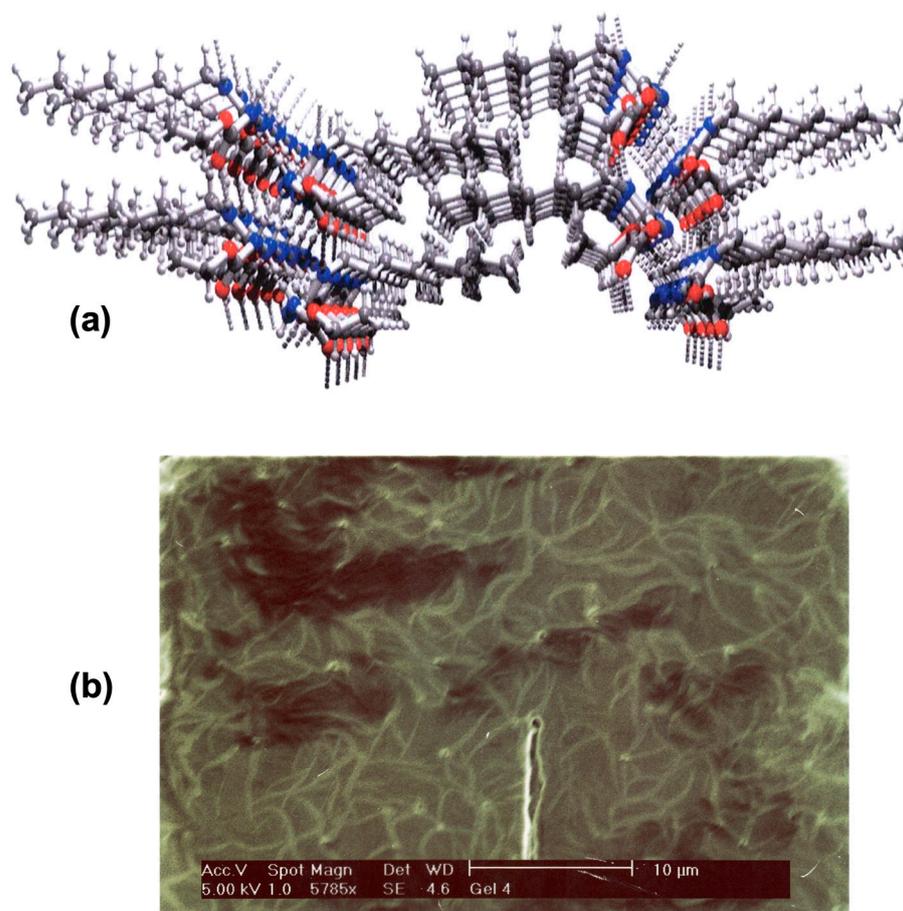
As already pointed out in the introduction, defects caused by sphere-like nanoparticles (colloids) lead already to a long-range interaction between the nanoparticles [12,42]. And this can already lead to a gelling of the low molar mass LC-matrix [12,19,20], transforming, e.g., low molar mass cholesterics into elastomeric materials [19]. In order to stabilize a director pattern in these elastomeric materials, the in situ formation of nanofibers/nanofibrils in the liquid phase showed itself, however, to be advantageous [5–9,21,43,44]. In this case, “gel forming agents” known from the gelling of (isotropic) liquids are added to the liquid crystalline material at higher temperatures. And during cooling they crystallize from the matrix, forming nanofibers/nanofibrils by self-assembly [6,8,45]. In the cases studied, the “gel forming agents” work in the liquid crystalline phase [5–10,21,43,46–48] as well as in isotropic liquids (Figure 2c). And the fiber structures obtained resemble that observed and studied in “polymer stabilized LC-phases” [14,34,49–51], in which the fibers are formed by polymerization of monomers in an LC-phase. Thereby, the (newly created) isotropic polymers phase-separate from the LC-matrix. Gelling is, however, reversible upon heating. Forming the nanofibers in the liquid crystalline phase thereby allows the nano-objects to adjust to the liquid crystalline director field and reduces the creation of defects in unwanted places, just because some nano-objects, e.g., colloids, are there [12,19].

Besides experiments for the reversible gelling of hydrogels [44,52], mostly two types of gel-forming agents were used to gel thermotropic LC-phases (see Figure 1). They are presented in Figure 3. They are trans-(1R,2R)-bis-(dodecanoylamino)cyclohexane [5,8,9,43,48] (commercially available) and various semicarbazides [6,7,21,45]. The semicarbazides were also designed to be photo-switchable [7,21] and they find interest in the context of a pathway complexity [53] because they can self-assemble in different ways. These compounds were studied for the gelling of isotropic liquids [6], for nematic phases [8,9,21,48] and for ferroelectric  $s_C^*$ -phases [5–7,21,43,46,47]. The chemical structure of the LC-materials to be gelled was quite different. For nematic materials, phenyl-bezoates, biphenyls, and “Schiff-bases” as well as commercial mixtures were used [8,9,21,48]. Concerning the possibility to gel quite different LC-materials, it is noteworthy that for ferroelectric  $s_C^*$ -phases “Felix mixtures” from the former Hoechst AG could also be gelled, which use hetero-atom (pyrimidine)-containing mesogens [21], whose lone electron pairs on the nitrogen atoms may compete with the H-bonding of the gelling agent and weaken its activity.



**Figure 3.** Chemical structures of gelling compounds used to gel liquid crystalline phases [5,6,21]. These are trans-(1R,2R)-bis-(dodecanoylamino)cyclohexane (upper part) and various semicarbazides without and with azo-groups [6,21]. On the right (b) pictures of a nematic mixture (left) and the same mixture gelled with the azo-semicarbazide 2 from (a) are shown. Part of the figure is taken from ref. [21].

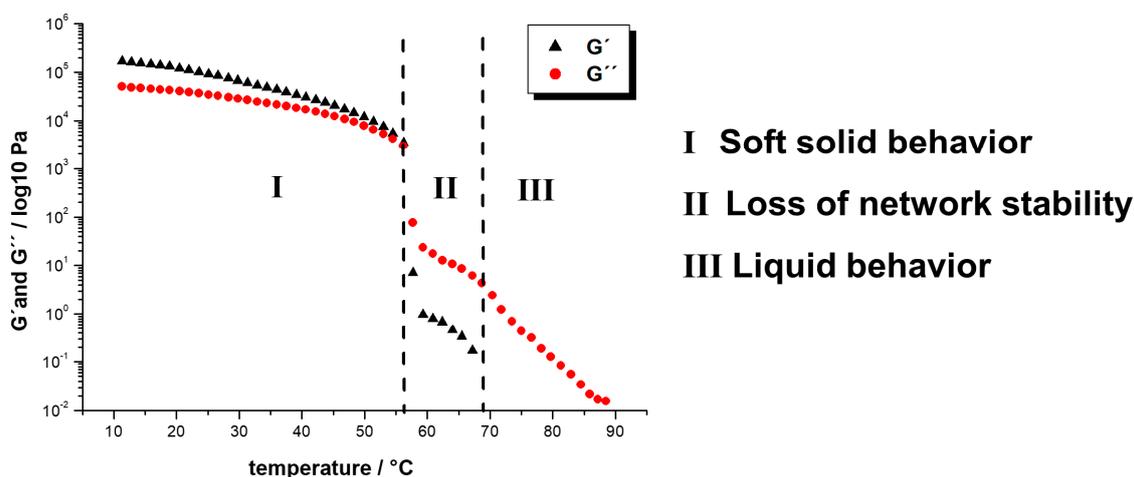
Trans-(1R,2R)-bis-(dodeca-noylamino)cyclohexane [5,8,9,43] is thereby a very strong gelling compound. Thus, it is possible to gel liquid matrices with a small amount of it (1 weight % or above). Since its gel-structure (see Figure 4) melts, however, at about 70 °C, only LC-phases with a clearing temperature well above 70 °C can be gelled in the phase. The semicarbazide based gel-forming agents show lower melting temperatures (about 55 °C) [6,7,21,45] (see Figure 4 for their packing motive) and are thus more flexible for the gelling of various LC-materials. Some of them can also be switched photochemically [7,21] from the trans state (leading to gelation) to the cis state (not gel-forming). They allow it thus to destroy (and reform) the gel within the LC-phase at a constant temperature. Their gel structure, which consists of fibers dispersed in the liquid crystalline matrix, can be visualized by SEM. It is presented in Figure 4, and it corresponds to structures described for “polymer stabilized liquid crystals” [34,49–51].



**Figure 4.** Packing motive (a) of semicarbazides (see Figure 3a) in the fibers, which form by self-assembly [6]. The oxygen atoms are marked in blue and the nitrogen atoms in red. In this way, each semicarbazide is connected to four neighbors and a ribbon is formed. (b) SEM-picture of a LC-phase gelled with trans-(1R,2R)-bis-(dodeca-noylamino)cyclohexane [5]. Pictures reproduced with permission of the Royal Society of Chemistry (a) and of Wiley-VCH (b).

Gelling of the samples can be measured easily on thick samples with low viscosity isotropic and nematic phases by detecting the increase in viscosity. A result from dynamic mechanical measurements is presented in Figure 5. It shows that the elastic modulus in the gel (below 55 °C) is larger than the imaginary part, describing the viscosity. Thus, the gel is a soft solid. Above the melting point of the gel, the viscosity is strongly decreased, but—at the same time—is now larger than the elastic component. By such measurements (heating and cooling), a reversible gelling can be detected [6]. For smectic phases, the detection of the gel point is not so easy, because of the high viscosity of the smectic phases

by themselves. And this problem becomes magnified for thin samples, as they are needed to study ferroelectric switching in  $s_C^*$ -phases. It is, therefore, very helpful that the addition of tiny magnetic particles [7] offers a way to detect gelling and its reversibility also for thin samples of highly viscose LC-phases. Such magnetic particles can be moved (accompanied by their orientation in lines) with an external magnetic field, if the sample “is Not” gelled. But they cannot be moved if gelling has happened. In this way, the reversible destruction of the gel by UV-irradiation and its reformation by irradiation with visible light can be studied [7].



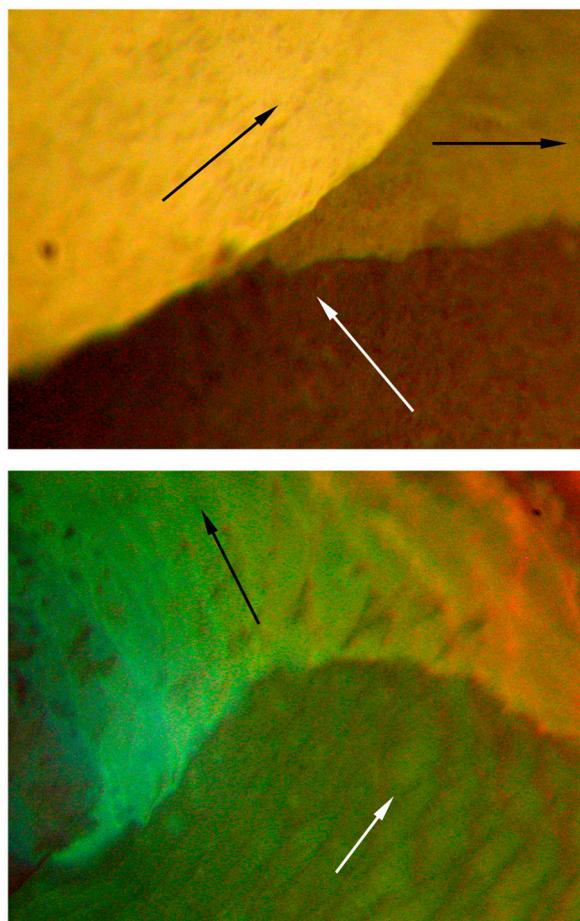
**Figure 5.** Measurement of the rheology of a liquid (1,2-dichlorobenzene) gelled with an azo-containing semicarbazide [6]. Below the melting point of the self-assembled gel-fibers (56 °C), the elastic properties dominate ( $G'$  larger than  $G''$ ). Above it, the viscose properties dominate and decrease continuously. Picture reproduced from ref. [6].

Switching experiments on samples gelled within pre-oriented LC-samples [5,6,8,9,21] shows that the fiber network of the gel stabilizes the director pattern present during gelling. It is, however, interesting that a switching/reorientation of the LC-director in an external field is well possible. This corresponds to the situation in “polymer stabilized liquid crystals” [34], which have a comparable morphology (see Figure 4). So, the coupling between the macroscopic network and the LC-director is weak. This is completely different from the situation in LC-elastomers, for which a switching/reorientation of the nematic phase in external fields was never possible [54], except for very highly swollen systems. In LC-elastomers, switching in electric fields could only be realized in ferroelectric  $s_C^*$ -phases with a nano-phase separation between mesogens and polysiloxane chains [22,35,36].

The comparison with “Polymer Stabilized Liquid Crystals” (PSLCs) is thereby instructive. PSLCs describe systems, in which a polymer network is formed within an anisotropic liquid crystalline matrix [14,34]. Thereby, a bi-continuous system is formed during the polymerization process, in which a continuous polymer network permeates a continuous liquid crystal phase. During the nano-phase separation order and structure of the liquid crystal phase are transferred onto the polymer network. It stabilizes mechanically the phase it was formed in. Such systems have attracted increasing interest [14,34], as they are serious candidates in the development of electronic paper, but also for the mechanical stabilization of smectic ferroelectric liquid crystals.

It is thus not surprising that switching experiments with gelled nematic and chiral  $s_C^*$ -phases were studied extensively, for nematics by Kato et al. [8,9,48] and for chiral  $s_C^*$ -phases mostly by Zentel et al. [5–7,21,43]. Overall, the gelled systems behaved thereby very similarly to “polymer stabilized liquid crystals” [34].

Detailed studies on the gelled systems were thereby conducted mostly in the form of freestanding smectic films (see Figure 6) [21,43].

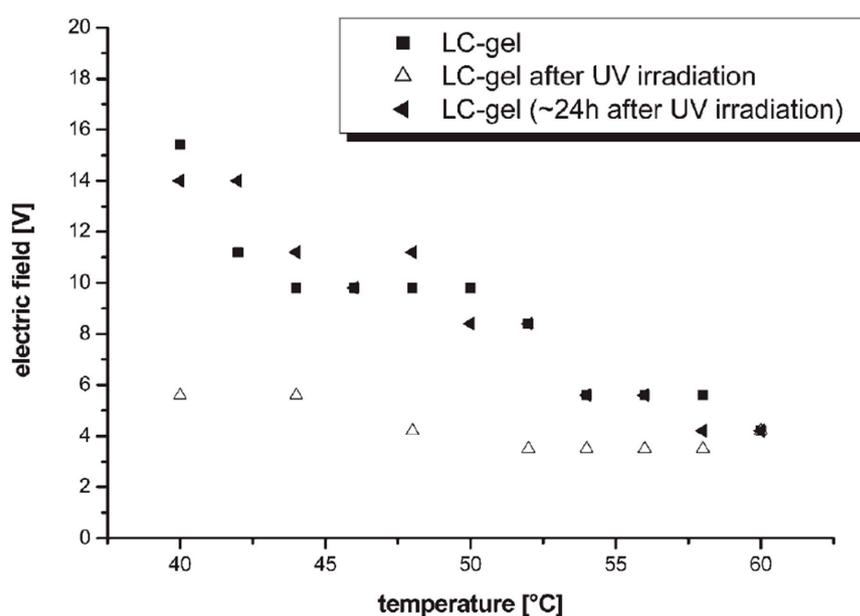


**Figure 6.** Optical microscopy of gelled freestanding smectic films [43]. The white and black arrows indicate the direction of the LC-director in different parts of the thin film; Picture reproduced from ref. [43].

In films cooled quickly below the gelling temperature, often a macroscopic two-phasic morphology consisting of highly gelled and a free liquid crystalline phase is observed [43]. However, slowly cooled samples look rather homogeneous (see Figure 6). Their films consist of different domains (many mm in size), which possess a different director orientation and sharp transition zones between the domains [21]. But these domains (with different director orientations) are again two-phasic, but are now on a smaller scale. They consist of a thin, fiber-like structure (dark), which cannot be switched and the majority of the sample, which can be switched/reoriented by the application of an electric field (applied in the plane of the film) [21]. So, clearly, the majority of the film consists of “free” LC-material, whose director pattern is stabilized by a fibrous structure. Considering the structure of the dark fibers, which stabilize the director-field, they cannot consist only of the pure “gel forming compound” because their volume is much too great for this (from the composition of the mixture the “gel forming compound” can contribute only to a few volume percent). So, in fact the fibers consist of the “gel forming compound” swollen with the LC-material.

Measurements to determine the equilibrium elasticity of the gel were prepared in the form of inflated bubbles [43,55]. These experiments showed, however, that the elasticity of the gel against inflation is not very large and larger forces can easily stretch/deform the gel irreversibly. This is opposite to the properties of covalently crosslinked LC-elastomers [55], which can withstand long-time mechanical stress. But it should be considered that gels—in general—are easily damaged by greater stress. On the other hand, dynamic mechanical measurements (Figure 5) show the effect of gelation clearly. In addition, the absence of movement of tiny magnetic particles in external fields proves the gelation (solidification) of

LC-phases [7]. Therefore, the gelled LC-phases have some mechanical stability, but they can be easily damaged by larger forces. This is in line with the observation that the elastic stabilization of the LC-phases by the gel is large enough to suppress electro-convection (manifested by flow/convection) [21], which gets induced by increasing electric dc-fields in the thin films (see Figure 7). Both rheology (Figure 5) and the onset of electro-convection (Figure 7) happen at the same temperature, but while rheology detects a change of several orders of magnitude, the change in the onset of electro-convection is much smaller (a factor of 2 to 3). But, obviously, each method measures something different. Rheology determines the macroscopic flow, which is directly determined by the percolated fiber structures of the “self-assembled gel-forming agent”. The onset of electro-convection determines movements in the director field, and they are determined mostly between the dark fiber structure rich in gel-fibers discussed above. In addition, the concentration of gel-fibers in the free-standing gelled smectic films may be smaller than calculated, because gel-fibers might concentrate in the meniscus, where the sample is thicker and less oriented.



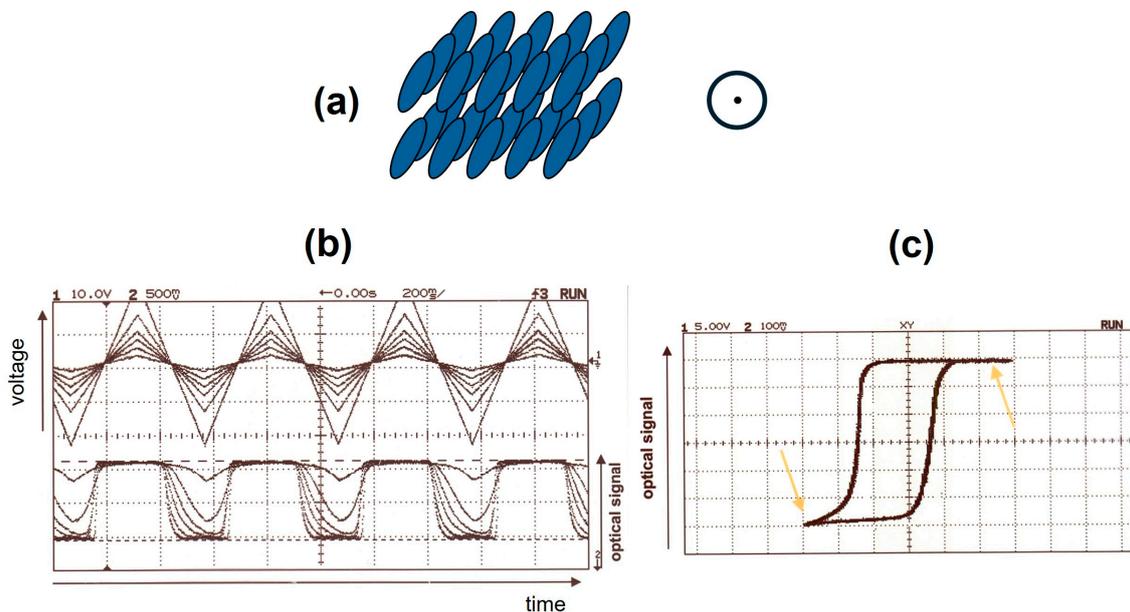
**Figure 7.** Temperature dependence of the onset-voltage of electro-convection [21] of smectic liquid crystals gelled with an azo-semicarbazide in the trans state, its modification after trans cis-isomerization and the situation after re-isomerization to the trans state (reformation of the gel). Picture reproduced from ref. [21].

The onset of electro-conversion (threshold field) depends on the amount of ionic impurities in the sample and on the film’s thickness. So, it cannot be compared between different smectic hosts (differences in ionic impurity concentrations), or between different films of the same smectic host, if the thicknesses of the films are different [21]. If, however, all external parameters are kept constant during the experiment, as in a photoisomerization experiment, changes in the convection parameters can be detected with great sensitivity. By this method it was thus possible to detect the photochemical removal of gelation (trans to cis isomerization) and its reversion (see Figure 7) [21]. For non-gelled samples (cis isomer, UV irradiation) the electro-convection starts at 4 to 5 V [21] independent of the temperature. For gelled samples it requires, however, more than 10 V to initiate electro-convection below the melting point of the gel (55 °C). It is thus possible to reverse gelling either by a temperature increase (melting of the gel) or by trans-cis isomerization (UV-irradiation).

Electric switching of the gelled LC-phases shows a modification to the switching process. Thereby—on one hand—the switching (reorientation of the LC-director) of nematic and chiral smectic C\* phases is slowed down [5,21,48] (this happens always for larger amounts (above 1 wt.%) of the gel-forming agent). This is reasonable as it corresponds to

the suppression of electro-convection discussed above. For very small amounts of some “gel forming agents”, however, sometimes an increase in the switching times has also been reported [5,48]. It may be that thin fibers in these gels disturb the director field at their surface and thereby facilitate the “on-set” of switching.

In addition, the director pattern present during network formation becomes stabilized. This is accompanied by the fact that the dark fibers in the medium (they are rich in the gel-forming agent, see Figure 6) do not switch [43], while the majority of the phase switches. This is well detectable for thin, free-standing films of gelled chiral  $s_C^*$ -phases [21,43]. It leads to the observation that (1) the ferro-electric hysteresis becomes unsymmetrical and two switching times (out of the stabilized state and back, into it) can be determined (see Figure 8) [21,43]. Thus, these gelled chiral  $s_C^*$ -phases behave like covalently crosslinked LC-elastomer with chiral  $s_C^*$ -phases [35,36] for which a stabilization of the director pattern—present during crosslinking—also gets stabilized. The use of photo-isomerizable “gel forming semicarbazides” allows it thereby to shift reversible—at constant temperature—between a gelled and a non-gelled system [21] in which one switching state is stabilized or not.



**Figure 8.** Asymmetric switching of gelled  $s_C^*$ -phases [5]. Above (a): schematic presentation of one switching state and the direction of the electric dipole (out of the plane); below: the electro-optic response (lower part) on variable external driving voltages (upper part) (b) and the ferroelectric hysteresis (c), which becomes asymmetric (compare refs. [5,35,36]). The orange arrows indicate the final switching state with the ferroelectric polarization pointing upward or inward in the display. Picture reproduced with permission of Wiley-VCH [5].

### 5. Further Perspectives including: Reversible Crosslinking

Now, what are the future perspectives of LC-materials, which combine elasticity and liquid crystalline ordering? LC-elastomers (as one class of such materials) are—even 40 years after their invention [28,33]—very popular, and recent reviews [22,25–27,30,31] focus on their use as mechanical actuators. They discuss, thereby, the different aspects for a “real world application” very critically [30] and highlight the importance of (i) a direct interaction with the surrounding medium [27] and (ii) the targeted incorporation of heating devices [31].

Gelled liquid crystals combine elasticity and liquid crystalline ordering too. However, they are mechanically not so strong and can easily be damaged by larger forces [21,43]. Therefore, they are not the prime candidates to prepare mechanical actuators. In addition, the direct contact with the surrounding medium might damage their structure, as

the gel-forming agents might dissolve and thus the structure might disappear. Since the interaction between the network structure and the LC-director is “weak” in “gelled liquid crystals” [34,49], their potential application should be more in the area to modify the switching of nematic and chiral smectic C\* phases. In addition, the combination of mechanical sensitivity and LC-properties can be useful in combination with cholesteric phases (mechanical modification of the selective reflection [37], lasing [37]) and in combination with ferroelectric chiral smectic C\* phases, where a mechanical deformation leads to piezo effects [36,39].

Another aspect, which will add a future perspective to gelled liquid crystals, is the reversibility of their crosslinking process. Recently, the general topic of reversible crosslinking has found a lot of interest in polymer chemistry. It is driven by the idea of the recycling of polymeric materials. In this context, all types of crosslinked polymer are problematic because they cannot be easily reprocessed. Now, materials like LC-elastomers are very special materials and used in tiny quantities. This makes their recycling less urgent than the recycling of commodities used in huge amounts. But, on the other hand, possibilities for a local rearrangement of the director field can be very advantageous for achieving and controlling a complex director pattern in LC-elastomers. And this is desirable for complex displays and is needed for obtaining complex shape variations in LC-actuators. Thus, crosslinking processes, which can be reverted or rearranged, find a lot of interest in LC-elastomers today [41,56–58]. The gelled LC-materials described above fall naturally into this category.

This is important because the natural equilibrium configuration of LC-elastomer networks is a polydomain state with a characteristic domain size of  $\sim 1 \mu\text{m}$ , unless special precautions are taken to cross-link the sample in an aligned configuration. However, such polydomain LC-elastomers cannot produce a macroscopic uniform actuation due to their lack of overall anisotropy. Therefore, LC-elastomers with uniform equilibrium molecular alignment, i.e., the monodomain or “single crystal” LC-elastomers [33], are needed to achieve a uniform (controlled) actuation. The primary achieved molecular alignment must be fixed afterwards permanently by network cross-linking. This is most commonly achieved through mechanical stretching during a two-step cross-linking process (a method introduced by Finkelmann [33]), because in this way large, but unidirectional, LC-elastomer samples were obtained at first. In addition, surface alignment on a substrate or cross-linking after shear extrusion can be applied. These methods can produce large, but unidirectional, LC-elastomer samples.

It is important to point out that all these approaches to produce permanently aligned monodomain LC-elastomers can be difficult to use in practice, especially if it is the goal to produce complex geometries and shapes of the elastomer. This is so because the required molecular alignment must occur before the final cross-linking reaction is completed. This is a natural result of the unavoidable competition between the alignment step (which needs low cross-linking/low viscosity to avoid quenched disorder effects) and the cross-linking step (this is needed to give the material mechanical stability but prevent further alignment).

Such reworkable LC-elastomers, in which the network structure can be rearranged, can be made by different concepts. Recently, mostly the use of reversible chemical bond formation has been under investigation [41,56–58] in so-called-“exchangeable liquid crystalline elastomers”. These LC-elastomer materials utilize dynamically cross-linked networks capable of reprocessing, reprogramming, and recycling. The chemistry used for this purpose and the specific reaction mechanisms that enable the dynamic, but covalent bond exchange are (1) trans-esterifications based on (1) hydroxyl- or (2) boronic-acids, as well as (chemically reversible) (3) polyurethane transcarbamoylation, (4) siloxane exchange reactions, (5) Diels–Alder dynamic networks, (6) disulfide exchange reactions, and (7) various cycloadditions.

In addition to these systems, which are based on covalent, but chemically reversible reactions, networks with nano-separated crosslinking points, which are held together by weak, reversible interactions, are also available. Such systems include LC-polymers,

solidified by netpoints held together by H-bonding [41]. The reversibly gelled LC-systems, described here, are very close to this last system.

**Funding:** This research received no external funding.

**Data Availability Statement:** No new data were created or analyzed in this study. Data sharing is not applicable to this article.

**Acknowledgments:** Alina Heck (MPI for Polymer Research, Mainz) is thanked for support in preparing this manuscript.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Van Esch, J.H.; Feringa, B.L. New Functional Materials Based on Self-Assembling Organogels: From Serendipity towards Design. *Angew. Chem.—Int. Ed.* **2000**, *39*, 2263–2266. [CrossRef]
2. Abdallah, D.J.; Weiss, R.G. Organogels and Low Molecular Mass Organic Gelators. *Adv. Mater.* **2000**, *12*, 1237–1247. [CrossRef]
3. Sangeetha, N.M.; Maitra, U. Supramolecular Gels: Functions and Uses. *Chem. Soc. Rev.* **2005**, *34*, 821–836. [CrossRef]
4. Fages, F. *Low Molecular Mass Gelators—Design, Self-Assembly, Function*, 1st ed.; Springer: Berlin, Germany, 2005.
5. Tolksdorf, C.; Zentel, R. Reversible Physical Network Stabilized Ferroelectric Liquid Crystals. *Adv. Mater.* **2001**, *13*, 1307–1310. [CrossRef]
6. Deindörfer, P.; Geiger, T.; Schollmeyer, D.; Ye, J.H.; Zentel, R. Semicarbazides as Gel Forming Agents for Common Solvents and Liquid Crystals. *J. Mater. Chem.* **2006**, *16*, 351–358. [CrossRef]
7. Deindörfer, P.; Davis, R.; Zentel, R. Photoresponsive Anisotropic and Isotropic Gels of Semicarbazide-Azobenzene Organogelators: The Use of Magnetic Polymer Colloids to Detect Gel-Sol Transformation. *Soft Matter* **2007**, *3*, 1308–1311. [CrossRef] [PubMed]
8. Kato, T.; Kutsuna, T.; Hanabusa, K.; Ukon, M. Gelation of Room-Temperature Liquid Crystals by the Association of a Trans-1,2-Bis(Amino)Cyclohexane Derivative. *Adv. Mater.* **1998**, *10*, 606–608. [CrossRef]
9. Mizoshita, N.; Hanabusa, K.; Kato, T. Fast and High-Contrast Electro-Optical Switching of Liquid-Crystalline Physical Gels: Formation of Oriented Microphase-Separated Structures. *Adv. Funct. Mater.* **2003**, *13*, 313–317. [CrossRef]
10. Kato, T.; Hirai, Y.; Nakaso, S.; Moriyama, M. Liquid-Crystalline Physical Gels. *Chem. Soc. Rev.* **2007**, *36*, 1857–1867. [CrossRef]
11. Zentel, R. Liquid Crystalline Elastomers. *Adv. Mater.* **1989**, *1*, 321–329. [CrossRef]
12. Petrov, P.G.; Terentjev, E.M. Formation of Cellular Solid in Liquid Crystal Colloids. *Langmuir* **2001**, *17*, 2942–2949. [CrossRef]
13. Al-Zangana, S.; Turner, M.; Dierking, I. A Comparison between Size Dependent Paraelectric and Ferroelectric BaTiO<sub>3</sub> Nanoparticle Doped Nematic and Ferroelectric Liquid Crystals. *J. Appl. Phys.* **2017**, *121*, 085105. [CrossRef]
14. Dierking, I. From Colloids in Liquid Crystals to Colloidal Liquid Crystals. *Liq. Cryst.* **2019**, *46*, 2057–2074. [CrossRef]
15. Stark, H. Physics of Colloidal Dispersions in Nematic Liquid Crystals. *Phys. Rep.* **2001**, *351*, 387–474. [CrossRef]
16. Thiruganasambanthan, T.; Ilyas, R.A.; Faiz Norrahim, M.N.; Muthu Kumar, T.S.; Siengchin, S.; Mohamad Misenan, M.S.; Ahmad Farid, M.A.; Mohd Nurazzi, N.; Muhammad Asyraf, M.R.; Syed Zakaria, S.Z.; et al. Emerging Developments on Nanocellulose as Liquid Crystals: A Biomimetic Approach. *Polymers* **2022**, *14*, 1546. [CrossRef]
17. Oswald, P.; Milette, J.; Relaix, S.; Reven, L.; Dequidt, A.; Lejcek, L. Alloy Hardening of a Smectic A Liquid Crystal Doped with Gold Nanoparticles. *Epl* **2013**, *103*, 46004. [CrossRef]
18. Thanassoulas, A.; Karatairi, E.; Cordoyiannis, G.; Kutnjak, Z.; Tzitzios, V.; Lelidis, I.; Nounesis, G. CdSe Nanoparticles Dispersed in Ferroelectric Smectic Liquid Crystals: Effects upon the Smectic Order and the Smectic-A to Chiral Smectic-C Phase Transition. *Phys. Rev. E* **2013**, *88*, 032504. [CrossRef]
19. Zapotocky, M.; Ramos, L.; Poulin, P.; Lubensky, T.C.; Weitz, D.A. Particle-Stabilized Defect Gel in Cholesteric Liquid Crystals. *Science* **1999**, *283*, 209–212. [CrossRef]
20. Roth, M.; D’Acunzi, M.; Vollmer, D.; Auernhammer, G.K. Viscoelastic Rheology of Colloid-Liquid Crystal Composites. *J. Chem. Phys.* **2010**, *132*, 124702. [CrossRef]
21. Deindörfer, P.; Eremin, A.; Stannarius, R.; Davis, R.; Zentel, R. Gelation of Smectic Liquid Crystal Phases with Photosensitive Gel Forming Agents. *Soft Matter* **2006**, *2*, 693–698. [CrossRef]
22. Ohm, C.; Brehmer, M.; Zentel, R. Application of Liquid Crystalline Elastomers. In *Advances in Polymer Science*; Springer: Berlin/Heidelberg, Germany, 2012; Volume 250, pp. 49–94.
23. Finkelmann, H. Liquid Crystalline Polymers. *Angew. Chem. Int. Ed.* **1987**, *26*, 816–824. [CrossRef]
24. Demus, D.; Goodby, J.; Gray, G.W.; Spiess, H.-W.; Vill, V. *Handbook of Liquid Crystals Volume 3: High Molecular Weight Liquid Crystals*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1998; pp. 1–556.
25. Brömmel, F.; Kramer, D.; Finkelmann, H. Preparation of Liquid Crystalline Elastomers. In *Advances in Polymer Science 250-Liquid Crystal Elastomers: Materials and Applications*; de Jeu, W.H., Ed.; Springer: Berlin, Germany, 2012; pp. 1–48.
26. Herbert, K.M.; Fowler, H.E.; McCracken, J.M.; Schlafmann, K.R.; Koch, J.A.; White, T.J. Synthesis and Alignment of Liquid Crystalline Elastomers. *Nat. Rev. Mater.* **2022**, *7*, 23–38. [CrossRef]

27. Pilz Da Cunha, M.; Debije, M.G.; Schenning, A.P.H.J. Bioinspired Light-Driven Soft Robots Based on Liquid Crystal Polymers. *Chem. Soc. Rev.* **2020**, *49*, 6568–6578. [[CrossRef](#)]
28. Finkelmann, H.; Kock, H.J.; Rehage, G. Investigations on Liquid Crystalline Polysiloxanes. *Die Makromol. Chem. Rapid Commun.* **1981**, *2*, 317–322. [[CrossRef](#)]
29. Terentjev, E.M. Liquid-Crystalline Elastomers. *J. Phys. Condens. Matter* **1999**, *11*, R239–R257. [[CrossRef](#)]
30. Lagerwall, J. Liquid Crystal Elastomer Actuators and Sensors: Glimpses of the Past, the Present and Perhaps the Future. *Program. Mater.* **2023**, *1*, 9. [[CrossRef](#)]
31. Zentel, R. LC-Elastomers: Structure-Property Relations and Concepts to Improve Applicability. *Liq. Cryst.* **2022**, *50*, 1129–1142. [[CrossRef](#)]
32. Petsch, S.; Rix, R.; Khatri, B.; Schuhladen, S.; Müller, P.; Zentel, R.; Zappe, H. Smart Artificial Muscle Actuators: Liquid Crystal Elastomers with Integrated Temperature Feedback. *Sens. Actuators A Phys.* **2015**, *231*, 44–51. [[CrossRef](#)]
33. Küpfer, J.; Finkelmann, H. Nematic Liquid Single Crystl Elastomers. *Die Makromol. Chem. Rapid Commun.* **1991**, *12*, 717–726. [[CrossRef](#)]
34. Dierking, I. Recent Developments in Polymer Stabilised Liquid Crystals. *Polym. Chem.* **2010**, *1*, 1153–1159. [[CrossRef](#)]
35. Brehmer, M.; Zentel, R.; Gießelmann, F.; Germer, R.; Zugenmaier, P. Coupling of Liquid Crystalline and Polymer Network Properties in Lc-Elastomers. *Liq. Cryst.* **1996**, *21*, 589–596. [[CrossRef](#)]
36. Gebhard, E.; Zentel, R. Ferroelectric Liquid Crystalline Elastomers, 1. Variation of Network Topology and Orientation. *Macromol. Chem. Phys.* **2000**, *201*, 902–910. [[CrossRef](#)]
37. Finkelmann, H.; Kim, S.T.; Muñoz, A.; Palffy-Muhoray, P.; Taheri, B. Tunable Mirrorless Lasing in Cholesteric Liquid Crystalline Elastomers. *Adv. Mater.* **2001**, *13*, 1069–1072. [[CrossRef](#)]
38. Vallerien, S.U.; Kremer, F.; Fischer, E.W.; Kapitza, H.; Zentel, R.; Poths, H. Experimental Proof of Piezoelectricity in Cholesteric and Chiral Smectic C\*-phases of LC-elastomers. *Die Makromol. Chem. Rapid Commun.* **1990**, *11*, 593–598. [[CrossRef](#)]
39. Brehmer, M.; Zentel, R. Ferroelectric Liquid-Crystalline Elastomers. *Macromol. Chem. Phys.* **1994**, *195*, 1891–1904. [[CrossRef](#)]
40. Meier, W.; Finkelmann, H. Piezoelectricity of Cholesteric Elastomers. 1. Influence of the Helicoidal Pitch on the Piezoelectric Coefficient. *Macromolecules* **1993**, *26*, 1811–1817. [[CrossRef](#)]
41. Lugger, S.J.D.; Houben, S.J.A.; Foelen, Y.; Debije, M.G.; Schenning, A.P.H.J.; Mulder, D.J. Hydrogen-Bonded Supramolecular Liquid Crystal Polymers: Smart Materials with Stimuli-Responsive, Self-Healing, and Recyclable Properties. *Chem. Rev.* **2022**, *122*, 4946–4975. [[CrossRef](#)] [[PubMed](#)]
42. Musevič, I.; Skarabot, M. Self-Assembly of Nematic Colloids. *Soft Matter* **2008**, *4*, 195–199. [[CrossRef](#)] [[PubMed](#)]
43. Li, J.; Stannarius, R.; Tolksdorf, C.; Zentel, R. Hydrogen Bonded Ferroelectric Liquid Crystal Gels in Freely Suspended Film Geometry. *Phys. Chem. Chem. Phys.* **2003**, *5*, 916–923. [[CrossRef](#)]
44. Herbst, M.; Dombrowski, M.O.; Preisig, N.; Dieterich, S.; Giesselmann, F.; Mésini, P.; Stubenrauch, C. Gelled Lyotropic Nematic Liquid Crystals. *Liq. Cryst.* **2023**, *50*, 1090–1100. [[CrossRef](#)]
45. Davis, R.; Berger, R.; Zentel, R. Two-Dimensional Aggregation of Organogelators Induced by Biaxial Hydrogen-Bonding Gives Supramolecular Nanosheets. *Adv. Mater.* **2007**, *19*, 3878–3881. [[CrossRef](#)]
46. Zhao, Y.; Guan, L. Use of a Gelator in a Ferroelectric Liquid Crystal: Pitch Compensation and Nanofibres. *Liq. Cryst.* **2003**, *30*, 81–86. [[CrossRef](#)]
47. Mizoshita, N.; Kutsuna, T.; Hanabusa, K.; Kato, T. Smectic Liquid-Crystalline Physical Gels. Anisotropic Self-Aggregation of Hydrogen-Bonded Molecules in Layered Structures. *Chem. Commun.* **1999**, 781–782.
48. Mizoshita, N.; Hanabitsa, K.; Kato, T. Self-Aggregation of an Amino Acid Derivative as a Route to Liquid-Crystalline Physical Gels-Faster Response to Electric Fields. *Adv. Mater.* **1999**, *11*, 392–394. [[CrossRef](#)]
49. Dierking, I. Polymer Network—Stabilized Liquid Crystals. *Adv. Mater.* **2000**, *12*, 167–181. [[CrossRef](#)]
50. Ma, C.; Wu, Y.; Yu, M.; Gao, Y.; Xiao, J.; Zou, C.; Yang, H. Effect of Liquid Crystalline Acrylates on the Electro-Optical Properties and Micro-Structures of Polymer-Dispersed Liquid Crystal Films. *Crystals* **2023**, *13*, 1294. [[CrossRef](#)]
51. Islam, M.S.; Chan, K.Y.; Thien, G.S.H.; Low, P.L.; Lee, C.L.; Wong, S.K.; Noor, E.E.M.; Au, B.W.C.; Ng, Z.N. Performances of Polymer-Dispersed Liquid Crystal Films for Smart Glass Applications. *Polymers* **2023**, *15*, 3420. [[CrossRef](#)]
52. Dieterich, S.; Prévost, S.; Dargel, C.; Sottmann, T.; Giesselmann, F. Synergistic Structures in Lyotropic Lamellar Gels. *Soft Matter* **2020**, *16*, 10268–10279. [[CrossRef](#)] [[PubMed](#)]
53. Contreras-Montoya, R.; Smith, J.P.; Boothroyd, S.C.; Aguilar, J.A.; Mirzamani, M.; Screen, M.A.; Yufit, D.S.; Robertson, M.; He, L.; Qian, S.; et al. Pathway Complexity in Fibre Assembly: From Liquid Crystals to Hyper-Helical Gelmorphs. *Chem. Sci.* **2023**, *14*, 11389–11401. [[CrossRef](#)] [[PubMed](#)]
54. Zentel, R. Shape Variation of Cross-Linked Liquid-Crystalline Polymers by Electric Fields. *Liq. Cryst.* **1986**, *1*, 589–592. [[CrossRef](#)]
55. Schüring, H.; Stannarius, R.; Tolksdorf, C.; Zentel, R. Liquid Crystal Elastomer Balloons. *Macromolecules* **2001**, *34*, 3962–3972. [[CrossRef](#)]
56. Saed, M.O.; Gablier, A.; Terentjev, E.M. Exchangeable Liquid Crystalline Elastomers and Their Applications. *Chem. Rev.* **2022**, *122*, 4927–4945. [[CrossRef](#)] [[PubMed](#)]

- 
57. Jin, B.; Yang, S. Programming Liquid Crystalline Elastomer Networks with Dynamic Covalent Bonds. *Adv. Funct. Mater.* **2023**, *33*, 2304769. [[CrossRef](#)]
  58. Pei, Z.; Yang, Y.; Chen, Q.; Terentjev, E.M.; Wei, Y.; Ji, Y. Mouldable Liquid-Crystalline Elastomer Actuators with Exchangeable Covalent Bonds. *Nat. Mater.* **2014**, *13*, 36–41. [[CrossRef](#)] [[PubMed](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.