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Liquid crystal elastomers in biological applications: a review

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ABSTRACT : This paper presents a review of the literature that deals with Liquid Crystal Elastomers (LCE) and focus on the recent progress in developing high performance application of liquid crystal elastomers materials for biological applications. In this paper, firstly we describe a brief history of liquid crystal materials comprising low molar mass liquid crystals, liquid crystal polymers, Oligomers and polymer dispersed LC. Then we explore the unique properties of LC elastomers for application in biology. These materials exhibit very rich elastic behavior as they couple elastic fields and mobile liquid crystal order. The liquid crystallinity of these solid LC allows these to shape change without any energy cost. The combination of unique properties, like soft elasticity and large spontaneous shape change, make them suitable to possess application in generic large scale actuators/ sensors and in biology like for the formation of artificial Muscles/MEMS/MOEMS. These promising results indicate that LCE materials will certainly plays an important role in the development of future applications and functional materials.

Keywords : Liquid crystalline phases, Spontaneous shape change, Soft elasticity,

I. INTRODUCTION

Liquid crystals (LCs) were first described by Reintizer and Lehmann in 1888. The liquid crystalline state, lying between the crystalline and the isotropic liquid states of matter, offers a broad range of applications where its anisotropic but liquid properties can be exploited [1-4]. Certain classes of organic molecules, micellar solutions of surfactants, main and side chain polymers and a large number of biological systems are known to show liquid crystalline behavior.

This paper at first briefly reviews the different types of liquid crystals focusing mainly on calamatic liquid crystals and then discusses in details the liquid crystals elastomers materials and their uses in biological applications.

II. LOW MOLAR MASS LIQUID CRYSTALS

1 Types of Liquid Crystals

A number of different types of molecules form LC phases when heated above their melting points. However, they all are anisotropic, they differ either in their shape or different solubility properties [3]. Derived from the shape of constituting molecules, we may differentiate the LC into three main categories: calamatic, discotic and banana shaped liquid crystal.

Calamitic Liquid crystals: The most common type of molecule that form LCs are rod shaped molecules (i.e. one molecular axis is longer than the other two) forming calamitic liquid crystal shown in Fig 1. Calamitic LC may be considered as the classical liquid crystals. The molecule should be fairly rigid at least for some portion of its length in order to maintain elongated structure. The best recipe for such a molecule is one or two ring structure attached directly or via some linking group and a hydrocarbon chain. However exceptions from this structure are also possible.

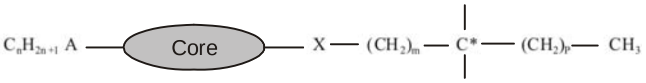


Fig. 1. A typical structure of a chiral, calamitic, rod-like liquid-crystalline compound. Where *n*, *m* and *P* are integers; (*B* + *m*) is the parity; *A* and *X* are polar groups; *Y* and *Z* are different substituents; * denotes a chiral centre.

Discotic Liquid Crystals: The compound made by Disc shaped molecules results in discotic liquid crystal shown in Fig 2. Disc like molecules possess one molecular axis shorter than the other two, however the rigidity in the central part is most essential again. The core of the molecule is usually based on benzene, triphenylene etc. with six or eight side chain usually resembling calamitic liquid crystals molecules.

Fig. 2. A general structural template for discotic.

Banana-shaped liquid crystals: Bent or banana-shaped liquid crystals represent a new sub-field of liquid crystals as shown in Fig 3. The existence of this type of LC depends on the length of the rigid core of molecules as well as on the magnitude of the bend and its position [5]. It is also found that achiral molecules with bent cores could form a chiral layer structure with a handedness that depends on the sign of the tilt and on the other hand. These materials, which form different phases are particularly interesting, because of their shape, they form a peculiar smectic phase in which the banana-shaped molecules are closely packed and are all aligned in the direction of bending.

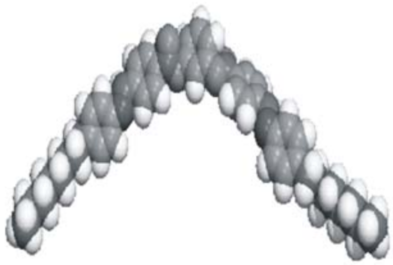


Fig. 3. Structure which formed by a typical banana shaped.

These LCs shows different phases with change in temperature or concentrations resulting in their further classification as Thermotropic and Lyotropic liquid crystals.

2. Liquid Crystals Phases

Friedel (1922) divided the LCs in three main categories: Nematic, Smectic and Cholestric [6-8]. The compound may possess only one or combination of these phase. When the solid is heated above its melting point to the isotropic phase, the smectic phase appears at low temperature whereas the Nematic phase appears just below the isotropic temperature. Calamitic liquid crystals are observed to show all phases. The Nematic phase is simplest phase of liquid crystals and shows thread like structure when viewed through the polarizing microscope. In this phase, molecules possess a preferred direction of orientation throughout the sample but no positional order as shown in Fig 4 and plate 1(a). There are various types of Nematic having slightly different properties base upon their molecular structure and chemical behavior. The two primary types of Nematic are uniaxial and biaxial. A biaxial Nematic is a spatially homogeneous liquid crystal with three distinct optical axes. This is to be contrasted to a simple Nematic, which has a single preferred axis, the director, around which the system is rotationally symmetric. The director has an arbitrary direction in space; typically impose by the outside forces like electric and magnetic field. The n and –n are equivalent and the molecules which from Nematics are either achiral or racemic.

Plate 1 (a)

Fig. 4. The molecules possess a preferred direction of orientation throughout the sample. There is no positional order.

Smectic phases, on the other hand, possess positional order in addition to the orientational order in Nematic liquid crystals i.e. the molecules maintain the general orientational order of Nematic, but also tend to align themselves in layers or planes. Motion is restricted to within these planes, and separate planes are observed to flow past each other. Many compounds are observed to form more than one type of smectic phase. As many as 12 of these variations have been identified and phases are divided depending upon the orientation of the director and positional order of the molecules within and among the layers e.g. Smectic A (SmA), Smectic B (SmB), Smectic C (SmC), Smectic D, Smectic E (SmE) etc. These names are given depending upon their order of invention. Out of these SmA and SmC are more common and were discovered earlier.

The simplest is the Smectic A phase made of non-chiral and non polar molecules by a one dimensional layered structure, in which each layer is essentially a two dimensional liquid Fig 5(a). This phase is uniaxial and the layers are incompressible and the long axes of the molecules in each layer, on an average, are perpendicular to the layer containing the molecules. SmC is similar to the SmA phase except that the director makes an angle other than 900 with the layer planes it is known as SmC phase. The tilt angle , that the long molecular axis makes with the layer normal is a strong function of temperature. In the case of a transition from the SmC to SmA, layer spacing at a temperature below the transition is given by

$$d(T) = d(T_{ac} \cos \theta).$$

The tilt angle is an order parameter for this phase. The LC phases with layering order of SmA [Fig 5(a) & Plate 1(b)] are known as non-tilted Smectic phases and with layering order of SmC [Fig 5(b) & Plate 1(c)] are known as tilted Smectic phases.

(*a*) Molecular arrangement in a SmA phase. The long axes of the molecules in each layer, on an average, are ⊥ to the layer containing the molecules.

(*b*) Molecular arrangement in a SmC phase, the director makes an angle other than 90° with the layer planes

Fig. 5.

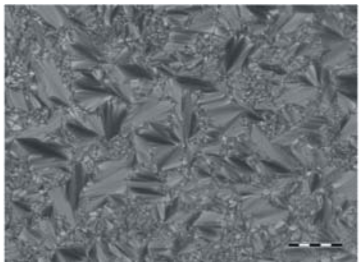


Plate 1(*b*) Smectic A

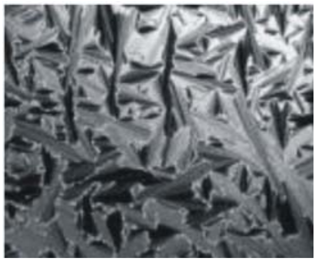
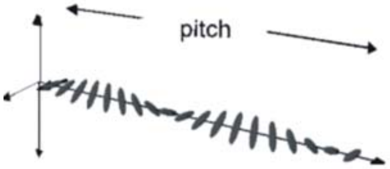
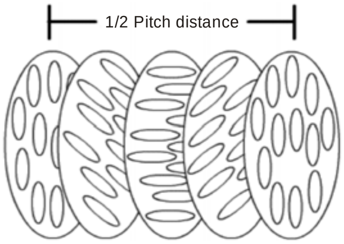


Plate 1(*c*) Smectic C

Molecular chirality has strong influence on the liquid crystal properties. The molecules having no mirror image symmetry are known as the chiral molecules. When these molecules are induced in the LC phases, a variety of new phases are formed that have very unusual properties [9-11]. Cholestric replaces Nematic phase and smectic phases are replaced by their chiral versions. Cholesteric Liquid Crystals does not possess any layered structure but director rotates in a helical fashion about an axis perpendicular to the long axis of the molecules. The pitch of N* is distance along which the director rotate by an angle 3600 [Fig.6 & Plate 1(d)]. However the structure repeats itself after half of the pitch due to equivalence of n and -n, where n is the unit vector along the director. These are also called chiral Nematic and are represented by N*



(*a*) Thepitch of the helix formed by cholesteric liquid crystal



(*b*) The rotation of directors in a continuous helical pattern about the layer normal.

Fig. 6.

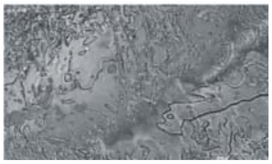


Plate 1(*d*) Chiral Nematic (Cholestric)

Chiral Smectic phases like SmC*, SmF* and SmI*, where long axis of molecule is tilted at an angle with respect to layer normal, can from different helical structures. In these phases, the director rotates around the cone generated by tilt angle as position of tilt along normal to layer is varied. The rotation of tilt is always in same direction for a given material and hence a macroscopic helix is formed. The chiral SmC helix phase is shown in Fig 7. It is the most common phase and is denoted by SmC* [Texture shown in Plate 1(e)]. Here, tilt angle ( ) is coupled with the layer thickness, whereas the azimuthal angle (angle between projection of director in the smectic plane and x-axis) is not [11]. There is no change in amplitude of tilt angle. The only variable that changes along the helix axis is the azimuthal angle. The periodicity of the helix is known as the pitch. It is temperature dependent but the variation behaviour changes from compound to compound. The helical structure of the material gives it interesting optical properties gets an unusually strong optical activity and a selective reflection can be seen in a quasi-homeotropically aligned sample. The symmetry of the SmC* phase permits the presence of spontaneous polarization, within layer plane and perpendicular to the director.

Fig. 7. The Helix formation in chiral SmC phase.

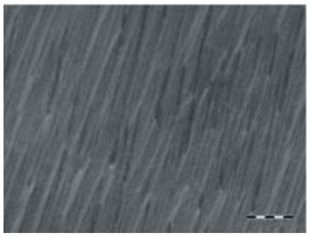


Plate 1(*e*) Chiral Smectic C

Similarly the discotic (disc like molecules) liquid crystals [Texture in Plate 1(f)] have basically two phases: Nematics and Columnar liquid crystal phases. The simplest one is the nematic phase in which the short axes of the molecules preferentially orient along a single direction called director. So in nematic phase there is orientational order but no positional order [2]. Positional order in discotic liquid crystals displays itself by tendency of the molecules to arrange themselves in columns. This means that in the plane perpendicular to the columns, the molecules tend to arrange themselves in a two-dimensional lattice either rectangular or hexagonal when they diffuse together. This is called columnar phase as shown in fig 8. These discotic systems can also be made chiral by incorporating a chiral unit into one or more of the peripheral units that surround the discotic core. Depending upon the structure of molecular orientation with respect to molecular axis and on lattice structure a number of columnar phases are distinguished. Similar way, banana shaped mesophase are denoted by the letter B, which refers to the characteristics bent or banana molecular shape. Literally the terms B1, B2, B3 etc. have been used to designate different phases as they were discovered. The distinction between theses phases was made on the basis of the optical textures and the different characteristics of the X-rays diffraction diagrams.

Fig. 8. The structure of nematic and columnar phases of disc like molecules.

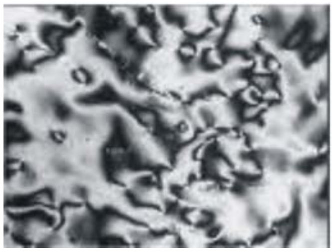


Plate : 1. (*f*) Discotic phase

3. Ferroelectricity in Liquid Crystals

In 1975, Meyer et al discovered the ferroelectricity in SmC* phase of liquid crystals [10]. These systems are important from the technical point of view due to their potential for applications as electro-optic media for displays and data processing devices. Meyer gave detailed explanation that the ferroelectricity of liquid crystalline materials depends strongly on molecular structure. When the SmC phase is constituted of achiral molecules then the environmental or space symmetry consists of a centre of inversion described as C2h. When the molecules of the phase are chiral the local symmetry in the layers is reduced to a polar C2 axis i.e. the chiral LC molecules break the point symmetry of the SmC phase from C2h (2/m) to C2 (2). This is one of the point symmetries allowing for ferroelectricity [12-13]. The time dependent alignment of the dipoles along the C2 axis causes a spontaneous polarization to develop along this direction, parallel to the layer planes, and therefore each individual layer has spontaneous polarization, which shows up in the direction of the two-fold axis. As the spontaneous polarization is coupled with director it also rotates. It will lead to cancellation of the microscopic polarization in the bulk sample, but each layer is spontaneously polarized. By suppressing the helix with electric field the phase will exhibit macroscopic polarization and a true ferroelectric phase is generated to get net spontaneous polarization (PS). So these are also known as helielectric materials. Conditions which are sufficient for the origin of PS may be satisfied not only in single compounds but in binary or multi-component mixtures as well. Ferroelectricity also exists in various classes of liquid crystals formed by discotic molecule. LC molecules possess Ferroelectricity in single component compounds as well mixtures. Single component systems gave appearance of spontaneous polarisation in any system having lamellar structure and consisting of tilted chiral and dipolar rod likes elements.

Since Meyer et al. discovered ferroelectricity in the chiral smectic C phase (smectic C*), it has been considered to appear only in doping chiral molecules which are used to reduce the overall symmetry of a liquid crystal mixture [11]. In the ferroelectric phase, dipoles are aligned parallel to each other, so that the system must have a polar symmetry. If the molecules could form a polar arrangement in their own systems, ferroelectricity may appear even in systems consisting of achiral molecules. The possibility of smectic phases with triclinic symmetry was predicted by De Gennes [4]. The phase was named Sm-CG (where G stands for "generalized") and was noted that it differs from its mirror image. This prediction had no experimental significance until the discovery of the ferroelectric smectic phases of bentcore (banana-shaped) molecules. Weissflog et al have reported that ferroelectricity could be detected only for one of the phases in some liquid crystals consisting of achiral banana shaped molecules. The existence of such phases depends on the length of the rigid core of molecules as well as on the magnitude of the bent and its position. This phenomenon is purely due to the shape of the molecules in case of banana shaped molecules. [5].

III. POLYMERIC LIQUID CRYSTALS

Another type of molecules that form liquid crystals is polymers [14-16]. It was expected that attachment of polymer backbone to LC could result in significant properties like increase of mesogenic ranges, presence of glass translation temperature etc. It leads to the synthesis of new class of LC known as Polymer Liquid Crystal (PLC) [14]. Mesogens (rod like, disc shaped or banana shaped molecules) must be incorporated into their chains. The placement of the mesogens plays a large role in determining the type of PLC that is formed. Main chain liquid crystals or MC-PLCs are formed when the mesogens are themselves part of the main chain of a polymer. Rigid elements are incorporated into the backbone of normally flexible polymers. These stiff regions along the chain allow the polymer to orient in a manner similar to ordinary liquid crystals, and thus display liquid crystal characteristics. Conversely, side chain liquid crystal polymer or SC-PLCs are formed when the mesogens are connected as side chains to the polymer by a flexible "bridge" (called the spacer) shown in Fig. 9. When mesogenic moieties form a structure necessary and sufficient for the ferroelectricity, spontaneous polarization (PS) appears in these materials. Flexible chain does not influence static parameters e.g. refractive index and magnetic susceptibility etc. However the presence of spontaneous polarization in the glassy state opens up the possibilities for investigation and technical application of pyroelectric and piezoelectric properties of corresponding solid films.

IV. OLIGOMERIC LIQUID CRYSTALS

Although a lot of research wok has been pursued in the field of monomers and polymer liquid crystals, but materials, which are intermediate between, the monomer and polymer are gaining interest [17-20]. These oligomeric materials are important from the viewpoint that they combine the mechanical behavior of polymer with the electro-optical properties of traditional molecular liquid crystal materials. These possess the properties of both monomer as well as polymer like large mesophase range, low glass transition temperatures and also overcome the difficulty of polymer liquid crystal like high viscosity, slow response time etc. Examples of the higher members of oligomers are scarce [20].

Ferroelectric Liquid Crystal Oligomers possessing chiral properties of the low molar mass liquid crystals have continued to fascinate the researchers since their discovery. Such interest stem not only from the applications of chiral liquid crystals materials in the thermo-chromic devices and the use of ferroelectric SmC phase in the electro-optic device applications but also results from their considerable fundamental importance as illustrated by the discovery of the blue phases and twist grain boundary phases. However, only the side chain liquid crystal oligomers are found to show the ferroelectricity.

V. POLYMER DISPERSED LIQUID CRYSTALS

In the recent years, a new class of materials popularly known as polymer dispersed liquid crystals (PDLCs) have shown a promise for using LC systems in large number of applications like switchable windows, privacy screens in offices, car sun roofs etc [21-24]. The principle of these systems is based on the matching of the refractive index of the polymer and LC material. The idea was conceived initially by De Gennes in 1979 and then studied by Ferganson (1984) and Doane (1986) shown in Plate 2 [22]. These PDLCs are the dispersion of LMM Nematic LC in the polymer matrix. The percentage of the LC in a polymer matrix varies from 2% to 70%. Conventionally such films are opaque in the undriven state and clear on the electrically driven state. Later Kitzerow in 1992, made use of chiral SmC LCs in PDLC devices, defined as polymer dispersed FLCs (PDFLCs), which are known for fast switching effects due to ferroelectricity showing response time of the order of few μS. They are useful for switchable and haze free displays. PDFLCs are having opened new possibilities of the materials for display applications.

Plate : 2. Texture of Polymer Dispersed Liquid Crystal.

VI. LIQUID CRYSTAL ELASTOMERS

As we have studied in the previous sections that the liquid crystals are unusual materials. They can flow but the spatial variation of the average molecular orientation direction is resisted by frank elasticity. Polymers too are unusual as they can show elasticity. Liquid crystals Polymers exhibit unique effects that are not simply the enhancement of the liquid crystals or polymers separately. Polymer liquid crystal, polymer chains with rigid anisotropic units, can order in a particular manner. These molecules expand when these component rods orient. A change of shape thus takes place, the effect however is very less. Linking the polymer chains together into a gel network fixes their topology and the melt becomes an elastic solid-a rubber. These materials are known as liquid crystals elastomers (LCE). In simple elastomers entropy change of polymers chains on relative movement of their cross-linked end points results in the elastic response. In LCE orientational order can be induced within these chains and its director can rotate independently of deformation of the cross-linking points. This is known as the Cosserat medium and one expects unique physical properties in it, especially for large deformations. Liquid crystal elastomers bring together three important ideas: orientational order in amorphous soft materials, responsive molecular shape and quenched topological constraints which helps to create many new physical phenomenons like extreme opto-mechanical effects, rotator mechanical coupling etc

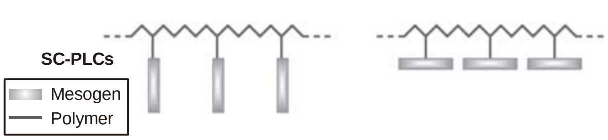


Fig. 9. Structure for MC-PLC and SC-PLC.

[25-28]. Liquid-crystalline elastomers are placed in a separate category from any other material on basis of physical properties.

Firstly, concept of these LCE was put forward by the P.G Gennes in 1975 [1]. However, the first side-chain LCE was synthesized by Finkelmann et al in 1981 [29]. For variety of LCE, Ringsdorf and Finkelmann [30-32] used polyacrylate backbones with a number of mesogenic pendants. These polyacrylate-based polymer chains have certain practical disadvantages like high glass transition temperature, low backbone anisotropy etc. However, polymers based on siloxane backbones show much higher chain anisotropy and are conveniently liquid crystalline at room temperature. The Cornell group has produced lightly cross-linked (i.e. rubbery without swelling) Nematic and smectic elastomers based on the rod-like mesogenic monomers connected via flexible spacers [33-37]. Another group of Nematic main-chain elastomers based on semi-flexible polyether chains have been prepared by Finkelmann and co-workers [38]. Lyotropic LCE system has also been synthesized in Freiburg [39].

Initially research was mainly focused on synthesis and some characterization work of LCE. In recent years, the emphasis is being given on to studies of new physical properties and the area of research into liquid-crystalline elastomers has been significantly broadened. Various researchers have studied the physical properties of these materials due to the growing ability of the research group to synthesize LCE, Finkelmann *et al* (1981) measured visco-elastic and opto-elastic properties as well as LCE behaviors in electric field [30]. Tajbakhsh *et al* (2001) report systematic study of uniaxial monodomain Nematic elastomers. They found that results are sensitive function of concentration of MC component [37]. Terentjev *et al* (2001) studied a wide range of photo sensitive materials based on azobenzene molecular moieties. They found that differing composition & topologies are reflected in varied mechanical response to radiations with ultraviolet light [38]. Finkelmann et al (2002) studied mechanical properties of monodomain side chain Nematic elastomers. They found that relaxation time is slowest relaxation time of network (as whole) and are consistent with hydrodynamics description of Nematic elastomers [39]. Dannio *et al* (2008) studied thermo-tropic and elastic properties of MCLCE by monomers and cross-linker molecular control. They found that choice of cross linker can be made according to behavior expected for materials [40]. In one way or other many new physical properties of these materials have been discovered. Theories have been formulated to describe the nature and properties associated with these materials. The main features of Cosserat-like rubber elasticity can be explained using the limit of continum linear theory [41]. This is fully applicable to a number of physical effects naturally involving small deformations e.g. acoustic waves or thermal fluctuations.

The orientational ordering properties of LC systems and the rubbery elasticity of polymer networks (Warner & Terentjev 2003) can be divided into two categories, depending on the LC phases exhibited by the systems, namely Nematic (Finkelmann et al) and Smectic LC elastomers (Lehmann *et al*). The spontaneous shape change and soft elasticity are two key phenomena in LCE that determine their physical responses and their potential for application in actuators [42]. The actuation mechanism is different for different type of LC elastomers. These phases and their application in actuators are discussed in detail in following sections.

1 Nematic LCE

The Nematic phase is simplest phase. Long polymer chains, with incorporated mesogenic units can order Nematically and form liquid crystal polymers. The rod character of molecules just changes little when they orient to form a Nematic phase. These molecules start elongate when their component rods orient. So there is a change of average molecular shape from spherical to spheroidal as the isotropic polymers becomes Nematic as shown in Fig 10. Nematic elastomers typically elongate spontaneously in the presence of Nematic (orientational) order, and reversibly contract when the order is lost (typically by heating). Nematic order can also be re-directed by electric fields or by boundary conditions and change the macroscopic shape. This change can be at low energy, so the phenomenon is called "soft elasticity" [56]. Theoretically predicted effect of soft elasticity, a remarkable phenomenon when there is no rubber-elastic energy (without any energy loss) in response to certain sets of strains, has been confirmed by several experimental findings. It is a large amplitude effect though there is a small threshold to director response. Director rotation proceeds and concludes in a singular manner during the low energy deformation.

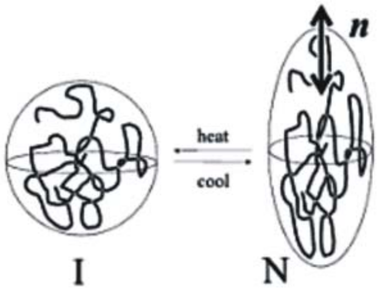


Fig. 10. Change of average molecular shape from spherical to spherioidal.

At the N-I transition temperature; there is a spontaneous shape change of the liquid crystal elastomers due to change of rotation of the liquid crystalline side chains. This shape change occurs nearly at a constant volume i.e. the molecule expands in one direction and contracts from other. This gives a flexing effect when the material is pinned on the substrate. This dramatic effect offers a door to use this material in artificial muscles/MEMS/ MOEMS.

Biological Applications of Nematic Liquid Crystal Elastomers

There have been a number of attempts to develop artificial muscle-like materials. These include piezo-electric, Ni-Ti alloys, conducting polymers, electrostrictive polymers, hydrogels and carbon nanotubes films etc. [43-48]. These actuator materials provide a wide range of stress, strain and response compared to the case of Skelton muscle. There are all smart materials but have considerable drawbacks at the moment. Piezoelectric actuators have a rapid response but the total strain is small, less than 0.1% and, as a result, complicated linkages are needed to get significant motion. Electrically conducting polymers show volume changes of a few percent but this is still much below that needed for a muscle. Shape memory alloys are promising but the response is slow and the life cycle limited. A soft-polymer actuator is the obvious analog for a muscle for fast but gentle manipulations. Nematic LCE due to phenomenon of soft elasticity are emerging as useful materials for biological application. A review on the work performed by various research groups in this field is given here.

Donald et al (2001) studied free-standing anisotropic side chain liquid crystalline elastomers films prepared using mesogens with laterally affixed polymerizable side chains [49]. They presented data on two networks: one containing the monomer of 4¢-acryloyloxybutyl 2,5-(4 butyloxybenzoyloxy) benzoate and another from a 50/50 mol % mixture of the above with 4-acryloyloxybutyl 2,5-di(4¢ pentylcyclohexyloyloxy) benzoate. They showed phase transition to be 30-45%. The order parameters of the oriented films were determined from the dichroic ratio of IR absorption at 3343 cm^{-1} to the inplane aromatic stretching overtone of the LC mesogen core. They showed that the variation of the order parameter with temperature scales similar to the strain changes at constant stress. From isostrain studies, conducted through the Nematic to isotropic phase transition, he shows that the two networks behave as true elastomers with significant differences in the force developed.

Liu *et al* (2006) developed a new kind of muscle-like material based on a network of side-on Nematic LC homopolymers. They used side-on LC polymers instead of main-chain LC polymers for synthesis reasons. These materials were thermo-responsive, with a typical contraction of around 35-45% and a generated force of around 210 KPa [50]. Subsequently, a photo-responsive material was developed, with a fast photo-chemically induced contraction of around 20%, triggered by UV light. They also prepared micrometer-sized artificial muscles.

Cladis et al (2000) studied Liquid crystalline elastomers (LCEs) composed of low molecular weight mesogenic units tethered to a cross-linked polymer network [51]. They have shown that due to remarkable shape changing properties in LCE at the Nematic-isotropic phase transition, they could serve as generic large amplitude, low frequency actuators and sensors i.e. artificial muscles. David *et al.* (2002) showed that fibrillar collagens and the dragline silks of web spiders belong to this remarkable class of materials [52]. The identification of these biopolymers as LCEs may have a predictive value. It may explain how collagens and spider dragline silks are assembled. It may provide a detailed explanation for their mechanical properties, accounting for the variation between different members of the collagen family and between the draglines in different spider species. It may provide a basis for the design of biomimetic collagen and dragline silk analogues by genetic engineering, peptide- or classical polymer synthesis. Biological LCEs may exhibit a range of exotic properties already identified in other members of this remarkable class of materials.

R. Zentel *et al* (2009) developed micrometer- sized actuators by heat micro-fluidic setup to prepare monodisperse spherical particles from liquid crystalline elastomers [53]. They were able to control their size by using experimental parameters between 280 and 550 Ωm. They found that when the particles are heated into the isotropic phase of the liquid crystal they show a strong and reversible shape change to a cigar-like conformation where the length of one axis is increased by up to 70%. They argue that the actuation properties of these particles are the result of uniform concentric alignment of the mesogens.

Muhoray *et al* (2002) studied that light can change the orientation of liquid crystal molecules and torque that causes reorientation originates in angular momentum transfer from radiation field to the materials. If a small amount of dichroic dye is dissolved in liquid crystal, a light induced torque can appear essentially without the transfer of angular momentum from light [54]. They show that in such cases, the dye molecules act as light driven molecular motors via an orientational Brownian ratchet mechanism, transfer angular momentum, which originates at the cell walls to the liquid crystal. The detail of this mechanism shows important applications ranging from flat-panel displays to opto-mechanical transducers.

Terentjev *et al* (2003) reported a significant electromechanical response in Nematic liquid crystalline elastomers filled with a very low 0.01% concentration of carbon nanotubes, aligned along the Nematic director at preparation [55]. They show that nanotubes create a very large effective dielectric anisotropy of the composite; their local field-induced torque is transmitted to the rubber elastic network and is registered as the exerted uniaxial stress of order 1 kPa in response to a constant field of order 1 MV/ m. They found that dependence of the effect on field strength, nanotubes concentration and reproducibility under multiple field-on and off cycles. The results indicate the potential of the nanotubes-Nematic elastomer composites as electrically driven actuators.

Finkelmann et al studied a new synthesis concept for LC-elastomers having the liquid crystalline units in the main chain as well as in the side chain. The main chain LC polymer used as cross linker is a LC-polyether which was previously synthesized. These new LC-elastomers shows spontaneous change in length at the Nematic to isotropic phase transformation temperature up to 300% which in dielectric elastomers (such as silicones) is found up to 30-40% [29].

From detail studies of review, we find that artificial muscles are human-made materials that have two main characteristics of real muscle namely, elasticity and contractility. These materials (artificial) muscles respond to various external stimuli (ion concentration, electric field, temperature, light, etc.) by a significant shape or size change. An ordered LCE with its anisotropic properties can provide an excellent frame work to mimic muscular action.

2 Smectic Elastomers

Smectic LCE have plane-like, lamellar modulation of density in one direction (SmA), or can have a tilt of the director away from the layer normal (SmC). Many other more complex smectic phases could exist in elastomers. The tilted SmC phase also exists in chiral forms which must be ferroelectric on symmetry grounds and so are their elastomers [56]. In smectic elastomers, the director cannot completely relieve both network and layer strain. So we expect that renormalized constant to be small but non zero and proportional to degree of Smectic order. The result of such coupling would be the rigid locking of uniform layer rotations. Experimental observations of deformations and ordering in smectic elastomers seems to support the idea of two-dimensional entropic rubber elasticity combined with a rigid response along the layer normal from the chain segments constrained between the layers. The strong effect of network shears of the uniform layer rotation has been reported and which is used to produce aligned monodomain Smectic rubbers. As already discussed, due to two phenomena, uniaxially aligned Nematic rubber will change its natural length in response to the change in degree of orientation order directly affected by the temperature, bias or optical field. Considering these facts, these materials have found importance in actuators. These characteristics are also expected in Smectic elastomers now. It is a very recent field of research and very-very few research groups are seemed to work over this topic.

VII. A LOOK TO FUTURE

The review of liquid crystalline elastomers concludes that there are several areas of fundamental interest for Physics and Biophysics in micro-gravity. Nematic rubber is already proved as an exciting system showing unique properties and the Smectic are expected to show unusual properties and applications. It is a new field just opening up to physical studies. Looking to the future many challenging problems are outstanding. Smectic LCE is yet to be studied in more details. The future work entails trying to develop Smectic LC elastomers to increase the overall sensitivity of detection and also to optimize the growth parameters to achieve best results. It is also expected to get these unique elastomeric properties using discotic and banana shaped molecules as the mesogenic units in polymers.

The other main issues that need to be examined when designing such a materials (actuator type) are the response time after an electrical pulse has been applied, the amount of strain achievable and if used in biological applications, the biocompatibility of the materials. LCE materials will certainly plays an important role in the development of functional materials like formation for artificial Muscles/MEMS/MOEMS. The probability is therefore large that qualitatively new directions as well as novel application potential in physics and biophysics could emerge.

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