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Liquid Crystalline Organic Compounds and Polymers as Materials of the XXI Century:
From Synthesis to Applications, 2011: 125-152 ISBN: 978-81-7895-523-0
Editors: Agnieszka Iwan and Ewa Schab-Balcerzak

5. Liquid crystallinity in polymers – Liquid crystalline epoxy resins

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Abstract. The present day materials science and materials technology are directed towards the development of task-oriented structures. Liquid crystalline polymers (LCP) are examples of such materials. Most of them contain mesogenic moieties essentially identical with those of the low-molecular weight liquid crystals. The properties of LCP depend on the structure of these polymers and the position of mesogenic groups within polymer molecules. The mesogens can be located along the main chain or extend sidewise of the chain. Combinations of these two have also been reported. It is possible to cross-link the liquid crystalline monomers or oligomers into a network that either retains the capability of undergoing phase transition involving a liquid crystalline state, or have the mesomorphic order frozen in at the curing stage.

In this report we discuss briefly the history of development and properties of thermoplastic liquid crystalline polymers and liquid crystalline polymer networks. The main part of our study is related to synthesis, properties and potential applications of liquid crystalline epoxy resins.

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Abbreviations

LCE	–	liquid crystalline elastomer
LCP	–	liquid crystalline polymer
LCPN	–	liquid crystalline polymer network
MC-LCP	–	main chain liquid crystalline polymer
SC-LCP	–	side chain liquid crystalline polymer
MC/SC-LCP	–	main chain/side chain liquid crystalline polymer
MC-LCE	–	main chain liquid crystalline elastomer
SC-LCE	–	side chain liquid crystalline elastomer
MC/SC-LCE	–	main chain/side chain liquid crystalline elastomer
SmC	–	smectic C phase
T_g	–	temperature of glass transition (vitrification)

Introduction

Materials capable of self-organization on the molecular level are of great importance in modern technology. An example of such materials are liquid crystalline polymeric systems, which combine typical features of liquid crystalline compounds, i.e. anisotropy of optical, dielectric, magnetic and other properties, with properties typical for polymers. Thermoplastic polymers built from linear and comb-like macromolecules are already relatively well known [1-10]. They are characterized by high impact resistance and high elastic modulus along the direction of molecular orientation. A few of them, despite of high price, found practical applications. Liquid crystalline polymer networks are another group of materials with interesting properties and many potential applications. Many studies have been devoted to elastomeric polymers of low cross-linking density, containing mesogenic groups in side chains. They are relatively easy to produce with a wide possibility of introducing significant structural modifications. Considerable attention is paid to cross-linked polymers with mesogenic groups in main chains and also to polymers obtained by curing liquid crystalline monomers, in which dense cross-linking results in ‘freezing’ the liquid crystalline phase. The thus obtained materials have a very high degree of order as well as mechanical and thermal resistance.

Uncrosslinked liquid crystalline polymers can form both thermotropic and lyotropic mesophase. Combination of properties of the anisotropic liquid crystalline systems with typical properties of polymers creates possibility of obtaining new materials having exceptional toughness needed in many special applications. Liquid crystalline polymers are characterized by several distinguishing features:

- very high strength, particularly in the direction of mesogen orientation,
- high elastic modulus in the direction of mesogen orientation,
- relatively low viscosity of precursors, melts or solutions,
- high chemical and fire resistance - due to ordered, compact structure,
- low solubility and resistance to solvents,
- high temperature of vitrification/melting,
- low thermal expansion coefficient resulting in high stability of shape and possibility of molding products with high dimensional precision.

Liquid crystalline monomers and polymeric precursors are also used to obtain anisotropic polymer networks. Much like in classic systems, permanent connections between chains cause significant changes in physical properties of the polymer. These properties depend on the structure of starting reagents and on the density of cross-linking. The mechanism and methods of obtaining such networks are analogous to those applied for classical polymer networks. Well-known curing reactions are used, with typical monomers and polymeric precursors. Depending on the type of reactive functional groups, curing can be initiated photochemically, thermally or by reactive curing agents. The main difference is that mesogenic groups are introduced into the molecules in the stage of precursor synthesis. The presence of these groups in the final product substantially affects the properties of the resulting material. This is because the precursor fragments can relatively easily be oriented and create ordered structures, which leads to anisotropy of physical properties.

Similarly to the classical covalent polymer networks, the LCPN have been divided into two groups, taking the physical state of polymeric chains as the criterion:

- polymers used in high elasticity region (liquid state), usually weakly cross-linked, referred to as the liquid crystalline elastomers (LCE),
- polymers used in glassy state (LCPN – liquid crystalline polymer networks), with ‘frozen’ liquid crystalline ordering, practically unchanging up to the degradation temperature.

1. Uncrosslinked liquid crystalline polymers

Liquid crystalline polymers are relatively new group of materials, though, according to Brostow [11], it was Vorländer, who first synthesized and studied many low molecular weight liquid crystalline systems, stating already in 1923 that polymeric systems can also have mesomorphic properties. Even earlier, in turn of the 19th and 20th century, Klepl, and

later Fischer, obtained a liquid crystalline polymer, a derivative of *p*-hydroxybenzoic acid, but they were not aware of unique properties of the obtained material. Only Vorländer, studying this polymer, discovered its mesophase. This is why Vorländer is often called the 'father'of liquid crystalline polymeric systems. Next information about liquid crystalline macromolecules was reported in 1937 by Bawden and Pirie. They studied solutions of tobacco mosaic virus and observed that elongated molecules a few thousand angstroms long form two separated phases, one of which, with higher polymer concentration, was characterized by optical birefringency [12].

However, studies on liquid crystalline polymers, both theoretical and experimental, have only started to be carried out more intensively in the 1950s. Flory in 1956 gave criteria of anisotropic phase formation, theoretically analyzing the behavior of rigid molecules in solutions. These criteria were relevant mainly to formation of mesophase in lyotropic solutions, but, by assuming the solution concentration of zero, they could also be applied to thermotropic polymers [13,14]. At the same time, a series of lyotropic polyglutamates was obtained at Courtaulds laboratory in Maidenhead, England, during research on synthesis of artificial silk, primarily on poly(γ-benzyl-L-glutamate) [15]. These systems, however, did not find wide practical applications, though a process of producing fibers from them was patented [16].

A breakthrough in the synthesis of liquid crystalline polymers was the achievement of Stephanie Kwolek from DuPont, who synthesized and managed to process lyotropic aromatic polyamides, poly(*p*-benzamide) [17] and poly(*p*-phenyleneterephthalamide) [18]. The latter is the well known Kevlar. Fibers formed from lyotropic solutions of these polymers have extraordinary mechanical properties, in particular high elastic modulus and high tensile strength. They are used for fabrication of protective wear including bulletproof vests and composites of very high endurance, which are key components of helmets and brake pads [9].

Initially, attention was focused on the properties of lyotropic polymeric systems. The most important group of such polymers are polypeptides and aromatic polyamides (besides the synthetic lyotropic polymers, also natural high molecular weight compounds soluble in water are known, as well, e.g. nucleic acids: DNA and RNA, collagen, cellulose and some viruses).

First reports on thermotropic polymers were published in 1960s, but mesomorphic character of the described systems did not stimulate a lot of interest at that time [19-21]. Intensity of studies on these polymers grew considerably in 1970s. They concerned the synthesis of linear copolyesters of ethylene terephthalate and 4-hydroxybenzoic acid [22] and those polyester

obtained in reaction of dicarboxylic acid chlorides with bis(4-hydroxy-acetophenone)azine [23]. The properties of these polymers confirmed the predictions by de Gennes, who suggested that main chain thermotropic liquid crystalline polymers could be obtained by introducing elastic fragments between rigid mesogenic groups [24, 25]. In the end of 1970s, further reports came out about the synthesis of comb polymers with mesogens in side chains [26-28]. Since then, the synthesis and studies on the properties and applications of thermotropic polymeric liquid crystals became more intense. Numerous types of such polymers were reported and described in many books and review papers published on the topic [2, 6-10, 29-34]. Most of the systems contained typical mesogenic groups which appeared also in the low molecular weight liquid crystals. Polymers not containing typical mesogenic groups were also found to form crystalline phases, often in a wide range of temperature. The examples are: polyphosphazenes ($–[RP=N]_n–$, R= ClC_6H_4O), polysiloxanes ($–[R_2SiO]_n–$, R= Et, n-Pr) and polysilanes ($–[R_2Si]_n–$, R = n-Bu) [35, 36].

A classifying criterion of liquid crystalline polymeric systems is the location of mesogenic group in the macromolecule. Mesogens can be introduced into the polymeric main chain (MC-LCP - main chain liquid crystalline polymer) or be present in side groups (SC-LCP - side chain liquid crystalline polymer). Synthesis of liquid crystalline polymers with complex structure has also been described, with mesogens built into both main chain and side chains (MC/SC-LCP). Schematic structure of some of them is shown in Figure 1. The liquid crystalline order can also be used as a criterion of classification of the materials, similarly as in the case of low-molecular weight compounds. However, the microscopic structure of smectic polymers is considerably different from classic smectics. A few examples of these structures, including different ordering schemes depending on the length of mesogens and flexible spacers between them, are shown in Figure 2 [7].

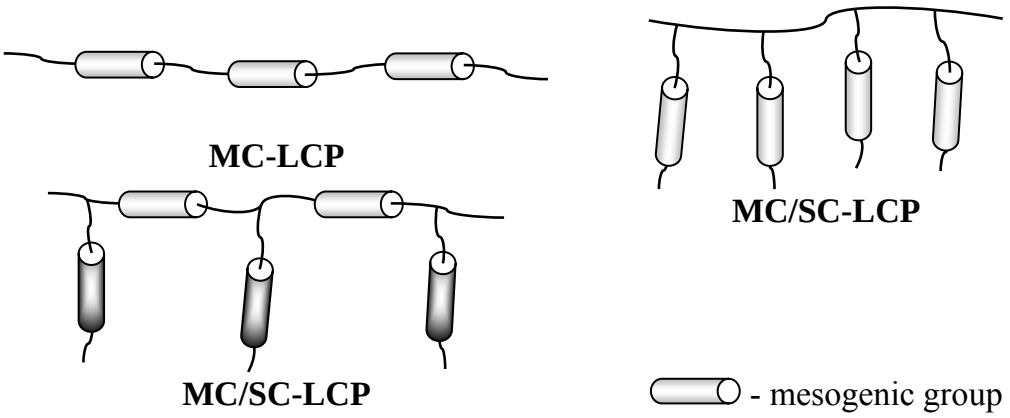


Figure 1. Possible location of mesogens in the macromolecule.

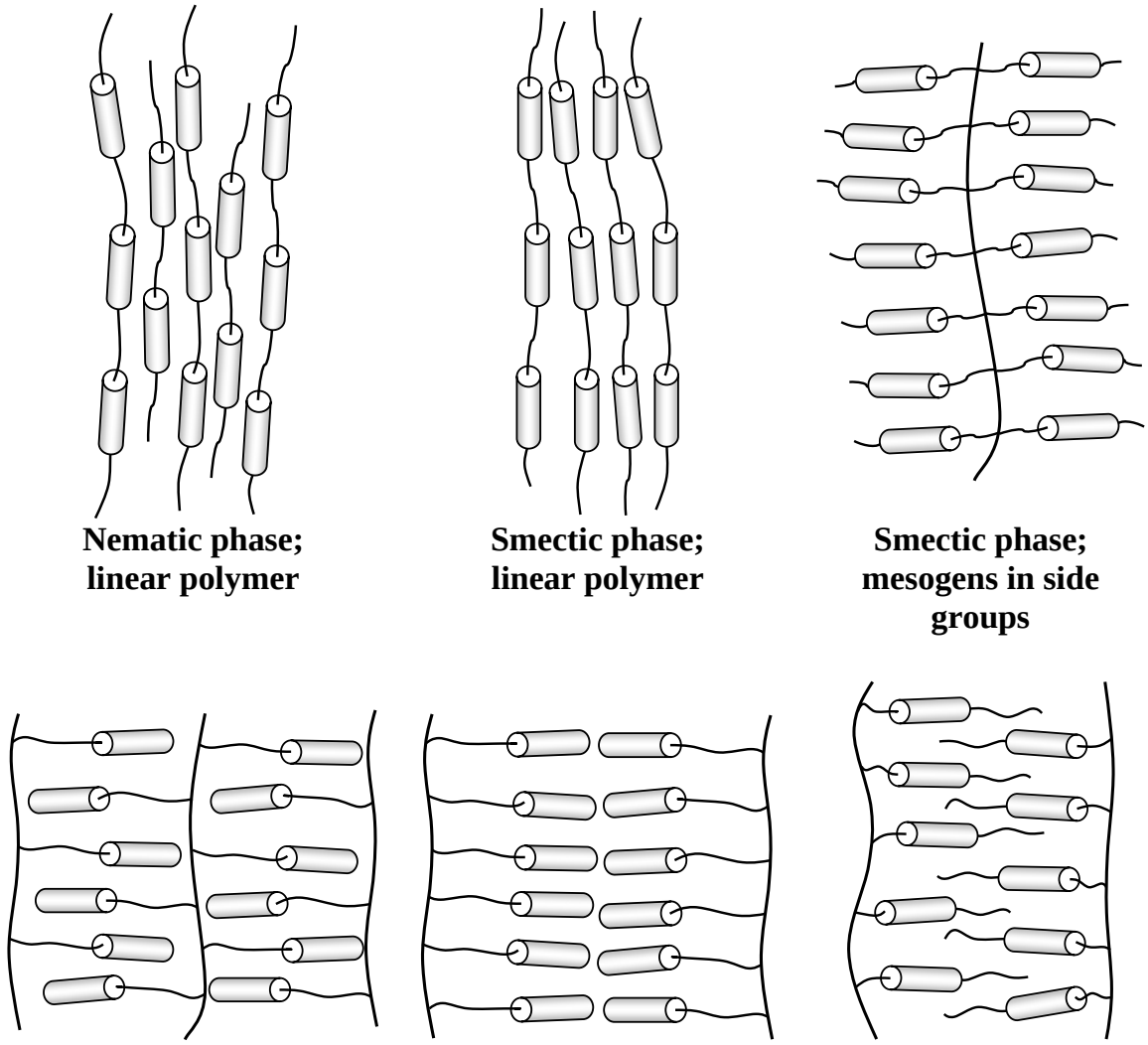


Figure 2. Basic types of ordering in liquid crystalline polymers.

Detailed classification, including mesogen types (discotic, rod-like) and their placement both in macromolecule and in ensemble, can be found in the literature [7, 11, 34].

1.1. Main chain liquid crystalline polymers (MC-LCP)

Polymers with mesogenic groups in the main chain are obtained mainly in polycondensation or polyaddition processes. These are most often liquid crystalline polyesters [1, 34, 37-41], polyamides [42-44], polyurethanes [45-47], less often polyethers [48-50], polycarbonates [51, 52], polyacethylenes [53, 54], or polyimides [55]. The fundamental structural components of main chain liquid crystalline polymers are rigid, rod-like and disc-like aromatic mesogenic groups similar to those present in the low molecular weight liquid

crystals. Direct linking of mesogenic groups would lead to materials of very high temperature of mesophase transition, typically very close to, or exceeding, the thermal degradation limit. For example, homopolymer of 4-hydroxybenzoic acid undergoes thermal degradation above 500°C, before even reaching the melting point [9, 35]. The main problem in the synthesis of such systems is to find a proper modification of their structure that would decrease the temperature of phase transitions without losing liquid crystalline nature of the product.

One possible method of such a modification is copolymerization of liquid crystalline monomers with comonomers which disrupt the regular structure of the macromolecule. Irregularity in the chain hinders crystallization, reduces crystallite sizes and partially hinders ordering of macromolecules, thereby lowering the temperature of devitrification/melting. This is a trick used in the production of a commercial copolyester of 4-acetoxybenzoic acid (ABA) and 2,6-acetoxynaphthene acid (ANA). The latter is known under commercial name Vectra A and manufactured by Ticona (formerly Celanese). Softening temperature of this copolymer is 280°C, i. e. lower than softening temperature of both ABA and ANA homopolymers. As the comonomers disrupting linearity, aromatic compounds substituted at ortho- or meta-positions, are frequently used, e.g. isophthalic acid or 2,5-substituted thiophene derivatives [9]. The nonlinearity and lack of structural regularity of the macromolecule may, however, adversely affect thermal stability of the polymer.

Another method of improving flexibility of macromolecules is to separate mesogens by flexible subchains (so-called spacers) which preserve linerality and structural regularity of macromolecules. These polymers are referred to as semi-rigid ones. Typical spacers are aliphatic hydrocarbon chains of various lengths, $–(CH_2)_n–$.

Introduction of substituents breaking linearity of para-substituted aromatic chains increases the distance between chains and weakens interactions between them. The density of chain packing is reduced. Random placement of the substituent can, however, disturb liquid crystallinity of the polymer.

Apart from the already mentioned polymer of the Vectra group (several types of aromatic copolyesters composed of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthene acid have been commercialized, all of which described with a common name Vectra [34]), large significance has a commercial polymer named Xydar, manufactured by BP-Amoco. Chemically, it is a copolyester containing terephtalic acid, 4-hydroxybenzoic acid and 4,4’-biphenol units, which can be processed by injection molding [34]. These polymers are characterized by high mechanical durability,

stretching resistance (due to chain orientation), low water sorption, impermeable by gases and high chemical resistance. Processing of polymers in liquid crystalline phase by extrusion or injection molding induces orientation of polymer chains in the direction of the flow. After cooling down, the product has well-organized structure and arrangement of molecules causes self-reinforcement. Extrusion method is used to produce plates, rods and fibers, whereas by press or injection molding one obtains construction supports, joints and switches used in microelectronics.

1.2. Side chain liquid crystalline polymers (SC-LCP)

Side chain liquid crystalline polymers were first obtained over 30 years ago. Of key significance for the synthesis of such systems were works of Finkelmann, Ringsdorf and coworkers [26, 27] and Shibaev [28], who were the first to obtain and study these polymers. A lot of essential information concerning side chain liquid crystalline polymers can also be found in the works of McArdle [5].

A flexible polymer chain in amorphous phase tends to attain coil-like conformation. In order to enable orientation of mesogenic groups introduced as branches, they have to be attached to the main chain by means of flexible spacers, which ascertain freedom of conformational motions of the parts of molecule and reduce stress between main chain and rigid groups in branches. Final properties of the system depend on the structure of the polymer main chain, the type of mesogenic groups, their density, and length of flexible spacers. The discussed systems usually have liquid crystalline properties similar to the properties of low molecular weight mesogenic precursors. Formation of polymeric structure often stabilizes the mesomorphic phase or increases the molecular order.

Liquid crystalline comb-like polymers are obtained primarily by homopolymerization of monomers containing side mesogenic groups, copolymerization of mesogenic and non-mesogenic monomers or copolymerization of different mesogenic monomers. Another method involves attaching low molecular weight mesogenic groups to the polymer chain by means of appropriate reactions, e.g. by hydrosilylation [4].

According to published data, rigid mesogenic groups are the most often attached to polysiloxane, polyacrylic or polymetacrylic chains, less often to chains such as polycarbosilane, polystyrene, polyether, polyester, polyurethane, polyphosphazene, etc. [3-7, 31, 32, 56-63].

Practical applications of liquid crystalline systems can be determined by their susceptibility to the orienting effect of an external force field. It turns out that polymers with side chain mesogens can be oriented, e.g. in a

magnetic field, much easier than the main chain polymers [34]. To date, many different comb-like systems have been described. They became the most popular objects of scientific research in the field. They can find applications in many areas of technology; as components of information storage systems, high-tech electrooptics, components of optical memory, optical filters and polarizers, in non-linear optics, holographic imaging or stationary phases in gas chromatography [5].

2. Liquid crystalline polymer network

2.1. Liquid crystalline elastomers (LCE)

Liquid crystalline elastomers, introduced as a theoretical concept by de Gennes [24, 25], are systems having low cross-linking density, with reversible phase transitions during heating or cooling. Above the glass transition (T_g), often equal to the temperature of transition into the liquid crystalline state, they become elastic and can be subjected to large mechanical deformations, during which mesogen orientation occurs or liquid crystalline order disappers. This is usually accompanied by changes in physical properties, e.g. transparency. In mesomorphic state, magnetic or electric fields have also the ordering effect. Preservation of the internal order can be achieved by lowering the temperature below T_g.

The synthesis and properties of LCE has already been a subject of several reviews and books [10, 64-71]. LCE are obtained from various liquid crystalline monomers. They primarily comprise polymeric systems into which reactive functional groups are introduced in quantities ensuring relatively low cross-linking density. Similarly to liquid crystalline polymers, LCEs are divided into elastomers with mesogenic groups in (i) side chains (SC-LCE), (ii) main chain (MC-LCE) and (iii) combined systems (MC/SC-LCE). In the last one the mesogenic groups (not necessarily the same) are found both in the main chain and in the branches (cf. Figure 3) [67, 70, 71].

In all liquid crystalline systems, of both low and high molecular weight, practical significance and applications rely on the possibility to enforce a long-range alignment of mesogenic groups and obtain a material with monodomain order. In the case of liquid crystalline elastomers, the parameter important for potential applications is the response to mechanical strain (e. g. change in transparency) resulting from changes in the arrangement of mesogenic groups. In branched systems with mesogens in side chains (SC-LCE), orientation of mesogenic groups can be modified relatively easily. The ability of mesogens to align and the dynamics of this process depends

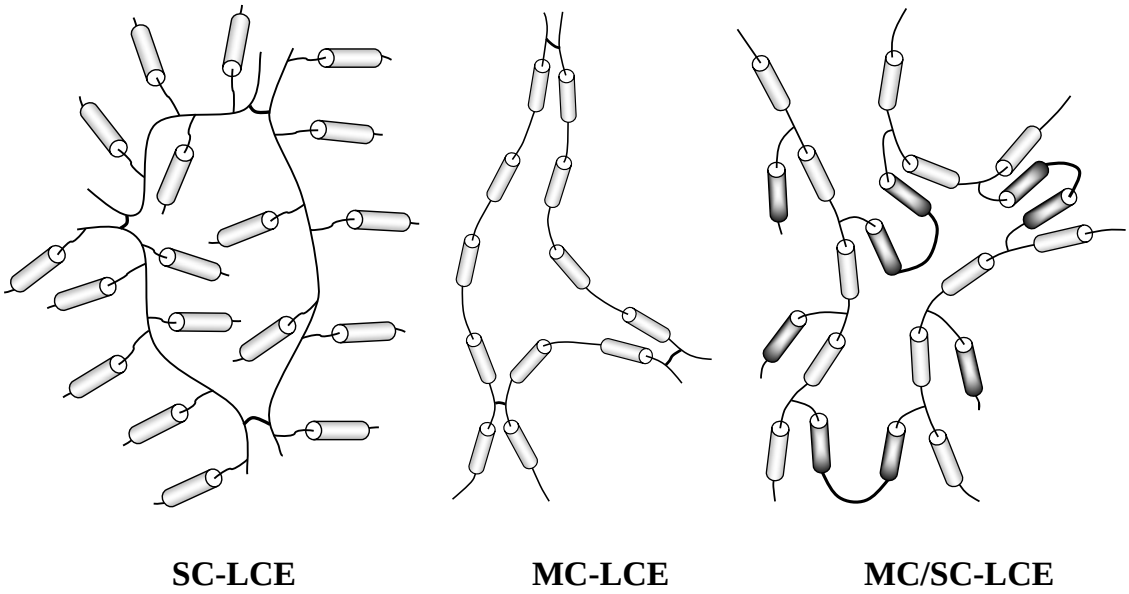


Figure 3. Types of structures in liquid crystalline elastomers.

mainly on the length of spacers and cross-link density. At low cross-link density, the side chains retain considerable freedom of motion. In elastomers with mesogens built into the main chain, mechanical strains also change mesogen orientation, like in SC-LCE, but these systems are harder to rearrange. In combined systems, the presence of mesogens both in the main chain and in side branches leads to a complex behavior under the influence of temperature and mechanical strains. These elastomers can be seen as a combination of two subsystems, whose properties strictly depend on the structure of the main polymer chain, mesogenic groups in branches and mutual interactions.

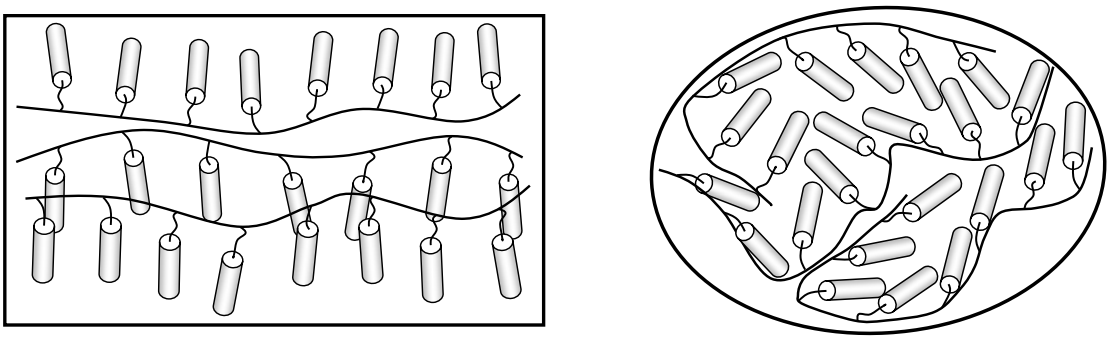
The earliest synthesized elastomers had mesogens in side chains. Continuing studies on the side chain liquid crystalline polymers, Finkelmann's group obtained a liquid crystalline elastomer using hydrosilylation reaction to produce polymeric polysiloxanes with mesogens in side chains. At room temperature, the product was opaque, typical for liquid crystals, and was also elastic. Mechanical deformation, e.g. stretching, caused reorientation of mesogenic groups, disappearance of turbidity and transition to transparent form [72]. Some liquid crystalline elastomers exhibiting internal order of SmC type can be heated up, stretched up to 300% of original length and cooled down, to retain the deformation. The system returns to the equilibrium state after re-heating which breaks the smectic order [73]. Liquid crystalline comb elastomers (SC-LCE) are also the systems with mesogens belonging to side branches in polyacrylate or polymethacrylate chains. Zentel and Reckert obtained such polymers by free

radical polymerization of acrylate and methacrylate esters containing attached mesogens and some amount of hydroxyl groups (5-8%) which were used to build cross-linking bonds in reaction with hexamethylene diisocyanate or 4,4'-methylene diphenyl diisocyanate. The liquid crystallinity did not change in the course of cross-linking. The elastomer exhibited the same type of mesophase as the polymeric precursor [74]. The majority of liquid crystalline elastomers with side chain mesogens produced nowadays have similar structure. The skeleton is polysiloxane, polyacrylic and/or polymethacrylic chain [5, 67, 69, 75-79].

In comparison with SC-LCE, the liquid crystalline elastomers with mesogens in the main chain were less studied. This is probably due to the necessity of running multi-stage reactions and a smaller range of potential applications. These systems were produced from linear liquid crystalline polymers obtained by solution polycondesation of mesogenic diols with allylmalonic acid or by melt polycondensation of the diols and diethyl allylmalonate. Cross-linking was carried out through double bonds in allyl groups, which reacted with Si-H groups in bifunctional α,ω-oligosiloxanes. The final elastomer featured a wide temperature range of mesophase and smectic order [74, 80, 81]. A technique of LCE synthesis with the use of liquid crystalline diepoxies was described by Giamberini and coworkers. It is based on a reaction of liquid crystalline diepoxy oligomers with dicarboxylic acids [82-85] or with aromatic amine [84]. Methods of synthesis of other main chain LCE were also given in a work by Xie and Zhang [67].

The first combined liquid crystalline elastomer systems with mesogenic groups appearing both in the main chain and in side chains were synthesized using a polymer precursor obtained by melt polycondensation or copolycondensation of mesogenic diols and diethyl malonate. This linear homo- or copolyester was then cross-linked by hydrosilylation, similarly to MC-LCE. The flexible aliphatic chains introduced during the cross-linking lowered the phase transition temperatures. The presence of mesogenic groups in the main chain and in side chains provided several types of liquid crystalline phases [74, 80, 81]. Synthesis of other combined LCE and their properties were also reported [70, 71].

The largest and most important group of liquid crystalline elastomers is that with mesogens constituting side branches. This is a result of relatively easy synthetic route and wide range of potential applications. Elastomeric polymer systems with introduced photoactive and photosensitive chromophore groups may also have large practical significance. Introducing chiral carbon atoms gives elastomers with ferroelectric and piezoelectric properties. Liquid crystalline elastomers may be potentially used as gas-separating membranes whose properties (gas permeability) strictly depend on temperature and



***T*<*T*isotropisation**
Mesogen ordering in the nematic phase forces the polymeric chain to align perpendicularly to the mean direction of mesogen orientation.

***T*>*T*isotropisation**
The nematic order disappears after heating up above the isotropisation temperature thus enabling relaxation of the polymer backbone to the coil-like conformation.

Figure 4. Schematic example of elastomer ordering below and above the temperature of transition to the nematic phase.

change in particular during transition from and to the mesomorphic phase. The sensitivity of LCE towards temperature, strain and magnetic or electric field enables application of these materials as waveguides, actuators, switches in optical devices, piezo- and pyroelectric sensors. The change of molecular arrangement in different temperatures is schematically shown in Figure 4. Attempts are made to use the effect of shape change due to heating (e.g. by an IR laser) or applying an electric field to create 'artificial muscles' for manipulating micro-objects attached to them [86]. The ability to form monodomain structures may be used in integrated optics, electrooptics, to obtain materials with nonlinear optical properties. Such materials can also be used in information storage systems, as polarizers, optical filters or oriented layers in displays [9, 64, 67, 71, 87].

2.2. Rigid liquid crystalline polymer networks (LCPN)

The interest in densely cross-linked liquid crystalline polymer materials results from the possibility of obtaining anisotropic solid systems with highly organized structure at the molecular level. This applies to polymers with T_g above the room temperature. Even though the term 'liquid-crystalline' suggests that these materials should be liquid, the term actually refers mainly to similarity of physical properties such as optical anisotropy or birefringence, which are characteristic for low molecular weight liquid-crystalline ordered structures. This order can be preserved in a reaction creating cross-linking bonds, amount of which is large in this case. As a

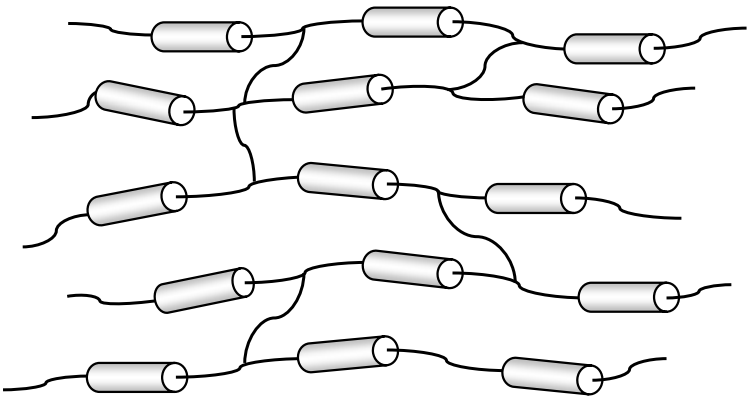


Figure 5. Schematic structure of a cross-linked liquid crystalline resin.

result rigid materials are obtained, stable practically up to the temperature of degradation. The presence of mesogenic groups also increases the mechanical durability.

First practical attempts to obtain polymer networks aimed at preserving the order characteristic for soaps. They were conducted by Herz with coworkers [88], by radical polymerization of a system containing natrium styryl undecanoate and water, using divinyl benzene as curing agent. In this process, a thin film was prepared with preserved smectic-like soap order. Similar attempts were described by Blumstein [89], who preserved pseudo (quasi) smectic order in a single layer of polar molecules by polymerizing tetraethylene glycol dimetacrylate.

The first 'true' liquid crystalline network, however, was obtained by Liebert and Strzelecki [90, 91]. Polymerization of mesogenic diacryl monomer of a type of Shiff base yielded a densely crosslinked material with preserved the structure characteristic for liquid crystals. It was stable up to degradation temperature [90, 91]. Further works of Blumstein's group dealt with polymerization of systems similar to those of Liebert and Strzelecki, but in a magnetic field. Cross-linking reaction produced material with oriented structure, as confirmed by X-ray studies [92].

In parallel with the synthesis of LCPN-type systems, theoretical research was carried out, to elucidate the structure and properties resulting from cross-linking. As it was mentioned already, deGennes predicted the possibility of obtaining cross-linked systems in his early papers on the structure of liquid crystalline thermotropic polymers [24, 25]. These studies were later extended e.g. by Warner and Edwards [93, 93]. Theoretical analysis led to the conclusion that rigid molecules linked by transverse bonds can form unique structures and have special mechanical properties.

Interesting properties and potential applications in high-tech technologies caused that many various LCPNs were designed and studied [9, 95-97].

Thanks to high thermal and mechanical stability, such systems can be used to produce foils for electronic integrated circuits and as matrices for advanced composites. They can become parts of optical switches, materials with nonlinear optical properties, waveguides, etc. In particular, their increased durability and impact resistance were found excellent.

LCPN are obtained mainly through cross-linking of low molecular weight liquid-crystalline monomers. The structure of a monomer corresponds, essentially, to the structure of low molecular weight liquid crystals. The molecule consists of rigid mesogenic groups and flexible side groups which must end with reactive functional groups to enable cross-linking. Length of the chains (spacers) linking the functional groups with the mesogen affects the rigidity of resulting networks. The length of spacers determines the elasticity and may lead to formation of the so-called semirigid-rod networks. Sometimes, the networks are also produced from monomers or oligomers which do not have liquid-crystalline properties by themselves, but contain rigid fragments which can induce anisotropic properties of the product through cross-linking [98, 99].

Cross-linking bonds can be formed during polymerization (self cross-linking), reactions initiated photochemically or thermally, or in reactions of monomers with curing agents. Photopolymerization is limited to materials of small thickness. Selection of curing conditions, particularly the temperature of the process, is limited by the range of liquid crystallinity of monomers. The largest amount of published information refers to liquid crystalline polymer networks obtained in reactions involving acrylates and methacrylates [96, 100-108], as well as isocyanate or cyanate [99-112], maleimide or nadimide [113-116], vinyl [117, 118], acethylene [119-122] and epoxy groups. In this report, special attention is given to liquid crystalline epoxy resins.

2.2.1. Liquid crystalline epoxy resins

Anisotropic polymer networks obtained by cross-linking of epoxy precursors fall among the most extensively studied groups of these materials. In the 1980s, methods of synthesis of several kinds of cross-linked systems were patented [123-125]. All were obtained from mesogenic monomers with terminal epoxy groups. These were diglycidyl ethers of 4-hydroxyphenyl 4-hydroxybenzoate, biphenyl-4,4'-diol and 4,4'-dihydroxy-α-methylstilbene, which were cured, like classic bisphenol A epoxy resins, using amines, sulphamides or anhydrides. The networks were reported to retain liquid-crystalline properties of the monomers, despite the presence of stoichiometric amounts of non-mesogenic curing agents.

Up to now, the synthesis of many epoxy monomers and oligomers with embedded mesogenic group was elaborated, their curing reactions were studied and formation of anisotropic structures was analyzed [84, 85, 112, 126-179].

Epoxy monomers used in the synthesis of LCPN-type systems have the structure typical for low molecular weight liquid crystals. The mesogen is usually formed by rod-like aromatic groups, to which flexible chains with terminal epoxy groups are attached (Figure 6).

Synthesis of the so-called twin mesogens epoxy monomers has also been described [95, 148, 156, 171], in which two mesogenic groups are separated by a flexible chain (Figure 7).

Examples of most common mesogenic groups found in liquid-crystalline diepoxy monomers are given in Table 1.

Methods of synthesis of the precursors, like those of bisphenol A epoxy resins, are based on the reactions of diol mesogens with epoxy compounds [84, 126-130, 137, 138, 140, 148, 152, 154-158, 161, 164-172], mainly epichlorohydrin. Less often, condensation is carried out of mesogenic dicarboxylic acids (usually, their chlorides) with glycidyl alcohol [135, 136]. These reactions are usually accompanied by formation of oligomeric homologues, but the oligomers can also be used to obtain LCPNs [140, 142]. Another method of introducing the epoxy ring is oxidation of mesogenic diolefins [132, 139, 141, 143, 144, 151, 159-163, 173-179]. The liquid crystalline properties depend on the length and flexibility of spacers connecting the mesogens with epoxy groups. The spacer length affects also the properties of the resulting polymer networks. In the case of systems produced in polycondensation reaction with epichlorohydrin, the length of flexible spacer is fixed. The method involving oxidation of double bonds provides greater flexibility of introducing spacers of different structure (e.g. aliphatic, oxyethylene) and arbitrary length. The length of the flexible chains facilitates orientation of molecules and lowers the phase transition temperature, but also reduces the degree of cross-linking and rigidity of

Figure 6. Molecular structure of a mesogenic epoxy monomer.

Figure 7. Structure of a twin liquid crystalline molecule.

Table 1. Mesogenic groups in epoxy monomers.

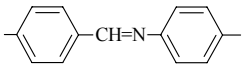
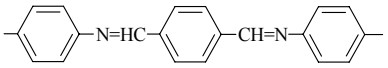
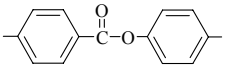
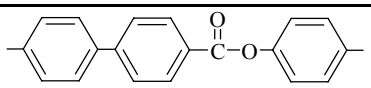
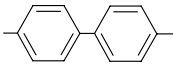
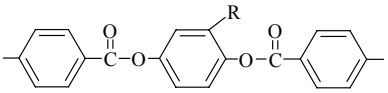
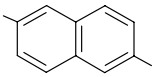
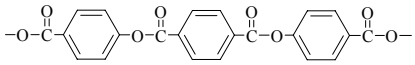
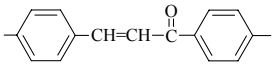
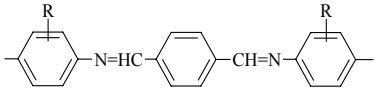
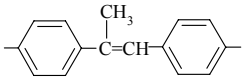
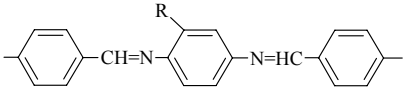
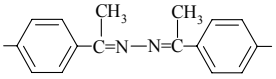
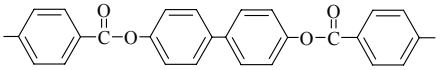
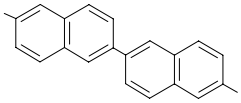
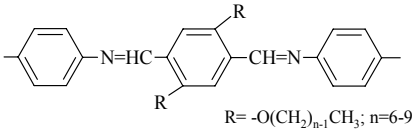
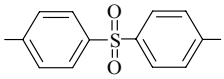
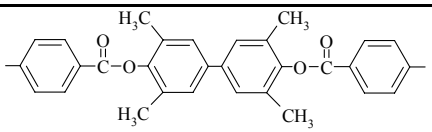
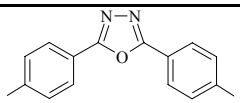
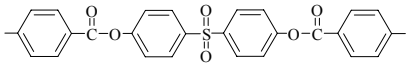
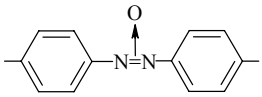
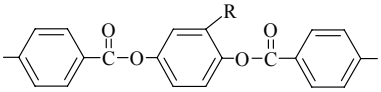
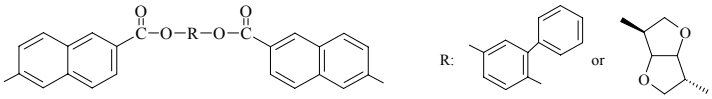
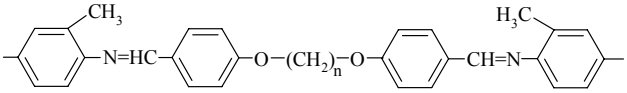
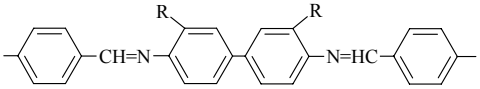
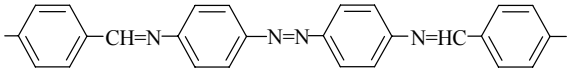
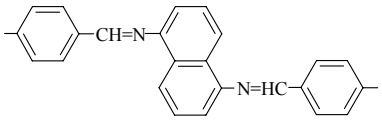
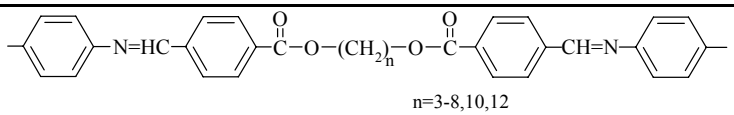
Structure	References	Structure	References
	[112]		[112, 152, 156]
	[112, 126, 128, 132, 141, 151, 153, 173, 178]		[126]
	[112, 126, 127, 138, 142, 143, 160, 165, 173]	 R= H, Cl, CH_3	[132-134, 137, 138, 144-146, 150, 159, 162, 173-175, 178, 179]
	[126]		[135]
	[126]	 R= H, CH_3	[138, 157, 158]
	[126, 127, 140, 146, 172]	 R=H or CH_3	[138, 161, 168]
	[126, 129]		[143, 176]
	[126, 130]	 R= $-O(CH_2)_{n-1}CH_3$; n=6-9	[154]
	[163]		[155]
	[166]		[163]
	[177, 178]	 R= $-COOC_nH_{2n+1}$; n=4,6,8,10,12	[164]
			[84]
 n=3-6			[156]
 R= H, CH_3			[161, 170]

Table 1. Continued

	[167]
	[169]
 n=3-8,10,12	[171]

network. By convention, the networks with aliphatic chains longer than 5 carbon atoms or with oxyethylene fragments are called the semi-rigid networks [9]. This classification is not, however, unequivocal, because the elasticity of a system depends also on the size and rigidity of mesogenic groups, the type of cross-linking reaction and kind of curing agents, hence on the density of cross-linking. These factors affect the concentration of mesogenic groups in the structure of the network. The majority of the known mesogenic epoxy monomers form nematic phase. This order is usually retained in the course of curing, though increase in the degree of ordering was also reported. Some monomers are capable of forming networks with smectic structure [95, 139, 140, 146, 180].

Beside the monomer structure, other factors have also an influence on the type of order emerging in the product. These are the temperature of the process (some reactions are exothermic), type of curing reaction and accompanying conditions, particularly the presence of external orienting force field (magnetic, electric) or surface properties of a mold (rubbing).

Cross-linking of mesogenic systems follows the same reaction paths as the curing of typical commercial epoxy resins. In the classical epoxy resins there are two kinds of functional groups which can take part in reactions leading to cross-linking: epoxy groups and secondary hydroxyl groups. The curing is usually carried out by introducing curing agents (hardeners) which become embedded into the network structure by means of polyaddition reactions. This role is played first of all by primary and secondary aliphatic amines, aromatic amines and dicarboxylic or multicarboxylic acids. Diphenols, polyphenols and polymercaptans were also used [181]. Functionality of hardeners affects the degree of cross-linking in the networks. It is also possible to use, as hardeners, compounds not containing active hydrogen atoms: Lewis acids (e. g. boron fluoride) or Lewis bases (e. g. tertiary amines). They act as initiators of cationic or anionic polymerization, respectively, but are not embedded in the network structure or used up during

the process. Acid anhydrides react with hydroxyl groups thus increasing the cross-linking density [181].

Similar methods are used for curing mesogenic epoxies, although the selected curing agent should ensure preserving the special nature of liquid crystalline systems. While selecting a hardener, one should bear in mind that it dilutes the polymer network particularly when it becomes a part of the network structure and may reduce T_g of the network. This is why aromatic hardeners are usually preferred. The majority of mesogenic epoxy monomers have a high phase transition temperature, which also determines the choice of appropriate hardeners. Curing agents should have rather a moderate reactivity. The reason is that conversion degree after heating the system up to the curing temperature should be low enough to enable spontaneous or external field enforced ordering of monomer molecules. Then, the curing reaction, usually exothermic, should not lead to heating up the system above the temperature of isotropisation or decomposition. The methods of producing rigid epoxy LCPN described in the literature encompass almost entirely curing with hardeners reacting at high temperatures (aromatic amines, phthalic anhydride and trimellitic anhydride), whereas curing with dicarboxylic acids yields products of low cross-link density and the properties typical for elastomers [82-85, 179] or systems resembling the main chain liquid crystalline oligoesters [182]. Cross-linked polymers were also obtained by anionic polymerization, using dimethyl dibenzyl ammonium chloride as initiator, or by thermal polymerization at high temperatures [136]. Another initiator used in anionic polymerization was 4-(N,N-dimethylamine) pyridyne [167, 169, 170, 175-177, 179]. In papers [169, 170] it was also reported that such a method of curing liquid crystalline epoxy precursors produces networks with anisotropic properties only when the precursor contains sufficiently long aliphatic spacers. Cationic photopolymerization of epoxy groups was also reported [132, 141, 151]. It provides a good control of the process and facilitates enforced orientation of mesogens (the molecules are oriented before polymerization). In ionic polymerizations, small quantities of initiators are used, usually not disturbing formation of the mesophase.

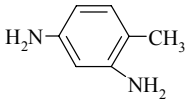
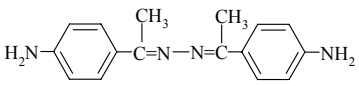
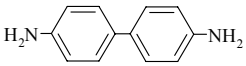
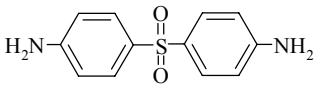
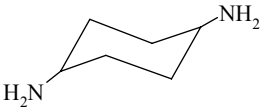
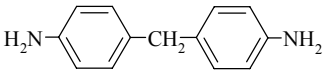
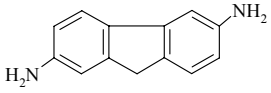
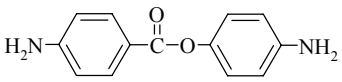
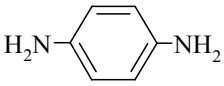
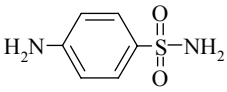
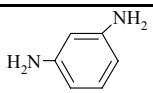
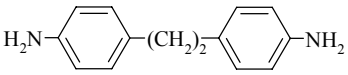
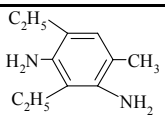
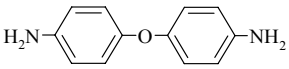
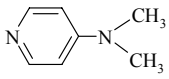
In the majority of the studies on curing of mesogenic epoxy monomers, primary aromatic amines were used [84, 112, 126-130, 133, 134, 137-140, 142-146, 148, 149, 152-172, 174-179]. They are rigid and have lower reactivity compared to aliphatic amines. The amines are built into the network structure and have to be added in stoichiometric amounts with respect to the epoxy groups. This is a significant mass contribution which can disturb the liquid crystalline order. Often, the system composed of a monomer and amine does not attain liquid crystalline state at all upon

heating, but in the course of the reaction one can observe, e. g. by polarized optical microscopy, the appearance of textures characteristic for mesophase. Tetrafunctional amines are most often used with two equivalent primary amino groups. Application of amines with two amine groups of different reactivity favors a change of order (e.g. a nematic monomer can yield a network with smectic order alignment [145]). The most frequently used aromatic amines used as curing agents are shown in Table 2. Anhydrides of dicarboxylic acids were used less often [130, 142].

By changing the curing conditions, the network structure and size of domains could be controlled. It is generally assumed that curing of liquid crystalline systems should be carried out within the temperature range of the mesophase. One must take into account here, that increasing the temperature within the mesophase range results in reduction of order. In many cases, at the beginning of the process, liquid crystalline phase may not appear, of all. This happens when stoichiometric amount of the hardener is added. However, during the reaction, the liquid crystalline structures eventually reappear. Sometimes, it is assumed that formation of a cross-linked structure encompasses three stages: propagation of linear chains, formation of branched structures and network formation (gelation). Upon heating, this process commences practically just after melting and it is a complex dynamic system, also depending on the homogeneity of the sample and individual properties of the components. Usually, the sample needs a post-curing at elevated temperature in order to increase the conversion of functional groups and reach the desired cross-linking density. This is typical for all types of epoxy resins. In photochemically induced crosslinking, the temperature of the process can be changed within the range of mesophase existence. The temperature applied is limited by the thermal stability of photoinitiator.

Samples cured without a force field yields mainly systems with polydomain liquid crystalline structure [158]. In order to take advantage of the properties resulting from anisotropy caused by the presence of mesogenic groups, the curing process should preferably be carried out by placing the sample in a magnetic or electric field, or on a specially prepared substrate. The curing process and formation of a rigid, solid structure preserves that order. Mechanical orientation, achieved in special cells with rubbing, also provides oriented materials, but of limited small thickness, only [141]. Lee and his group demonstrated that curing of liquid crystalline epoxy resin on carbon fiber induced an anisotropic alignment in the cured product [146]. The degree of order can be further improved by applying additional electric field [183]. Curing in a magnetic field was also carried out. Fields of strength varied from 1.45 to 13.5 T were used [133, 134, 136, 150, 157, 168, 174, 180, 184]. The magnetic field ensures orientation of mesogens in the entire sample

Table 2. Amines used as curing agents of liquid crystalline epoxy precursors.

Structure	References	Structure	References
	[84, 112, 126, 127, 167-171, 175, 177]		[126, 129]
	[112, 133, 134, 137, 150]		[126, 130, 142, 143, 146, 148, 149, 154, 155, 159, 161, 166, 168]
	[126, 128]		[134, 137, 138, 140, 148, 149, 152-154, 156, 159-161, 164, 166, 168, 174-176, 178, 179]
	[126, 165]		[137, 143-146]
	[138, 148, 154, 161, 175]		[145, 168, 172]
	[158]		[157]
	[162]		[159, 161, 163, 166]
$H_2N-(CH_2)_6-NH_2$	[168]		[167, 169, 170, 175-177, 179]

and yields systems with order parameter of around 0.8-0.9. The system cured in magnetic field has a monodomain structure which is arranged along the applied field [157, 178]. These systems have excellent thermal conductivity in comparison with other polymer materials [157]. The fracture toughness of the polydomain system was higher than that of the isotropic one. The bigger was the domain size and higher order parameter, the better was the fracture toughness [158].

On the other hand it was also reported that lateral substituents in mesogens can decrease some mechanical properties including tensile strength, Young modulus and elongation at break [164].

The liquid crystalline diepoxy precursors can also be used to prepare advanced composites with selected fillers. Synthesis and properties of materials prepared from liquid crystalline epoxy resins and fillers, e.g. diphenyl aluminum phosphate nanorods [176], polyhedral oligomeric silsesquioxane [179], carbon fibres and nanotubes [185, 186], organoclays [187] and polyaniline nanorods [188] were described. The polyaniline

nanorods also played a role of curing agent. It was shown that addition of this nanofiller improved thermal stability and electrical conductivity of composites. By blending liquid crystalline epoxies with anisotropic fillers, one can induce preordering of the filler particles and equip the resulting materials with unique physical (optical, electrical) properties. Properties of composites with carbon fiber prepared from a liquid crystalline epoxy resin were compared with those from bisphenol A diglycidyl ether [185]. The hardener was 2,4-diaminotoluene. The dynamic-mechanical studies showed that the composite with liquid crystalline precursor had higher T_g, superior fracture resistance and higher elastic modulus. Jang and Lee reported that addition of liquid crystalline epoxy resin to diglycidyl ether of bisphenol A caused reinforcement of the latter. T_g was also higher [189]. The reactive filler from the polyhedral oligomeric silsesquioxane group increased rigidity of the composite in glassy state and reduced T_g [179]. A small quantity (2%) of diphenyl aluminum phosphate nanorods added to a liquid crystalline epoxy matrix resulted in substantial growth of its vitrification temperature [176]. These results suggest that liquid crystalline epoxy resins can be used as matrices for advanced composites. An example of such a composite provides the material with uniform, ordered structure of nanofillers, obtained by monodomain orientation of the polymer matrix.

Summary

Special properties of epoxy LCPN described here result from a combination of liquid crystalline features with properties typical for cross-linked epoxies, i.e. low thermal expansion coefficient, high durability and chemical stability, as well as very good mechanical properties. This is why the liquid crystalline epoxy resins have been extensively studied as materials for high-performance composites, electronic packaging, insulating layers, and for nonlinear optics. Their potential practical significance stems from applicability in electronics, optical, aviation and space industry. Epoxy resins are obtained in most cases from low molecular weight monomers. When melted, they have low viscosity and can be used for filling complex molds, and also as protective coatings for electronic chips. The use of low molecular weight monomers to obtain polymer networks facilitates ordering the molecules in a force field during the process of curing and manufacturing of materials having high degree of uniform order.

Acknowledgements

We thank Prof. Henryk Galina for helpful discussions on the manuscript.

Financial support of Structural Funds in the Operational Program - Innovative Economy (IE OP) financed from the European Regional Development Fund - Project *Modern material technologies in aerospace industry*, No. POIG.01.01.02-00-015/08-00 is gratefully acknowledged.

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Liquid-crystalline epoxy resins as matrices for composites and nanocomposites. Article. Mar 2012.Â Uncrosslinked and crosslinked liquid-crystalline polymers exhibit increased fracture and breaking toughness, high modulus of elasticity (especially in the direction of mesogen orientation), very good barrier properties, low coefficient of thermal expansion as well as specific optical, electrical and thermal properties. They can be used as matrices in composites for particularly demanding applications, in the electronics and aerospace industries. This article is a review of the literature related to the synthesis and selected properties of composites and nanocomposites prepared from liquid-crys... Our line of powerful Liquid Epoxy Resinsâ€“including Bisphenol A, Modified Bisphenol A, Bisphenol A/F, Modified Bisphenol A/F, Bisphenol F offers the reliability, protection and performance you need, backed by the local customer support Only Olin can provide, virtually anywhere in the world. Liquid Epoxy Resins. View Products. Product Name & Description.Â D.E.R.â„¢ 301. Modified liquid epoxy resin; compared with standard bisphenol A based liquid epoxy resin, similar viscosity, improved flexibility, longer pot life and anticorrosion performance; suitable for high solids (80% volume solid above) formulation. Modified Bisphenol A Liquid Epoxy Resins. 245 â€“ 265. 10,000 â€“ 14,000. Computing crystallinity. âˆ†V. Liquid of known density and thermal expansion coefficient. Polymer. %C = v âˆ’ vamorphous partially crystalline v âˆ’ vamorphous totally crystalline. Dilatometry. Youyong Li and, William A. Goddard III Macromolecules 2002 35 (22), 8440-8455.Â Example: Highly crystalline polymer with no orientation of crystallites. Diffraction spots are blurred into full circles. What if itâ€™s not crystalline?