Liquid Crystalline Polymers

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In this chapter, liquid crystalline polymers are defined, methods for their characterization are described, and some examples of liquid crystalline polymers are discussed.

20.1 The Liquid Crystalline State

Solid bodies in which elementary building blocks (atoms, molecules, ions) are arranged regularly and at geometrically precisely defined points in a lattice are called crystals. The defined structure prevails throughout the whole crystal and is also referred to as *long-range order*, referring not only to the position of the crystal building blocks but also to their orientation in relation to the crystal lattice (long-range position and orientation order). This order means that the crystal has a regular structure at a macroscopic level and generally anisotropic mechanical, electrical, and optical properties. By contrast, most liquids are only locally ordered. Thus, a degree of order can only be considered in terms of one or two molecular diameters at most, and the physical properties are independent of direction; they are *isotropic*.

The transition from an ordered solid body to a disordered liquid can be achieved either by melting the body or by dissolving it in a suitable solvent. Most crystalline solid materials transition directly from an ordered state into a disordered, liquid state when heated above their melting point or dissolved. However, a number of substances, under certain conditions, form an additional state—that of an anisotropic liquid. On the one hand, this phase exhibits the typical characteristics of a liquid, that is, it has a more or less viscous flow behavior. On the other hand, its physical properties are anisotropic, typical of crystals. As the physical properties of this phase lie somewhere between those of a crystal and those of an isotropic liquid, it is referred to as *liquid crystalline* or *mesophase*. A substance that can form a mesophase is called *mesogenic*. The three-dimensional position and orientation long-range-order present in the crystal is partially lost in this phase. The formation of this kind of liquid crystalline phase is also known as *mesomorphism*.

If the transition of a pure substance from a crystalline state to a mesophase is caused by a change in temperature, then the mesophase formed is referred to as a *thermotropic* mesophase. Liquid crystalline phases, which are transformed into a mesogen by adding a solvent, are called *lyotropic* mesophases. *Amphotropic* substances can form both kinds of mesophases.

20.2 Lyotropic Liquid Crystals

So-called lyotropic phases are two- or multi-component systems made up of a solvent, amphiphilic compounds, and, often, water. Lyotropic mesogens are often typical soaps, such as the alkaline salts of long-chain fatty acids or quaternary alkyl ammonium compounds with at least one long alkyl chain, but can also be polyhydroxy compounds and carbohydrates that have been modified to make them, in part, water repellant.

The dissolved amphiphiles form micelles in certain temperature and concentration ranges. The shape of the micelles is strongly dependent on the solvent and the shape of the amphiphilic molecules and can vary greatly, with the resulting shapes ranging from spheres and cylinders to double-layered shapes (▣ Fig. 20.1).

Micelles are usually able to move around freely when the surfactant concentration is low. As long as this is the case, these liquids are not referred to as liquid crystals. If the

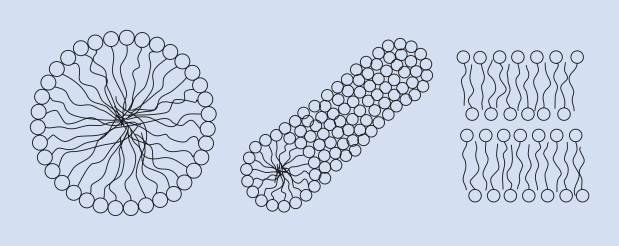


Fig. 20.1 Examples of the different shapes formed by amphiphilic molecules. (**a**) Spherical micelle (*left*). (**b**) Cylindrical micelle (*middle*). (**c**) Double layer lamella (a mesophase)

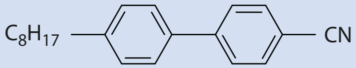


Fig. 20.2 4′-Octyl biphenyl-4-carbonitrile—an example of a thermotropic liquid crystalline material

concentration of amphiphile is greater the micelles become organized into more highly ordered liquid crystalline phases and superstructures.

With changes in temperature or concentration the mesophases can transform into one another. Such transformations are reversible.

20.3 Thermotropic Liquid Crystals

Thermotropic liquid crystals do not directly transition from a crystalline into a liquid state when heated. Instead they pass through one or several additional phases within limited and well-defined temperature ranges. These phases often have anisotropic physical properties, such as those that can occur in crystals; however, they exhibit flow behavior. A well-known example is 4′-octyl biphenyl-4-carbonitrile (Fig. 20.2) which undergoes transition into a liquid crystalline state at 22 °C and then transforms into an even less ordered mesophase when heated further to 34 °C. The transition into an isotropic melt only takes place at 41 °C.

The thermotropic liquid crystalline state typically, but not exclusively, occurs in compounds with pronounced molecular anisotropy. This means that this state often occurs in compounds made up of molecular rods (calamatic mesogens) or discs (discotic mesogens). Several selected structural varieties are shown in Fig. 20.3.

20.4 Liquid Crystalline Structures

Typical liquid crystals are characterized by an orientational order of their anisometric molecules and a partial or complete destruction of the positional foci of their molecules. In the simplest case the orientational order is maintained, such as the orientation of the long axes of rod-shaped *calamatic* molecules in small regions, so-called *domains*. The molecular orientation found in *nematic* or *cholesteric* calamatic phases are shown schematically in Fig. 20.4.

The rod molecules’ centers of gravity are statistically distributed in the nematic phase. However, all molecules are orientated in one preferential direction, the *director*.

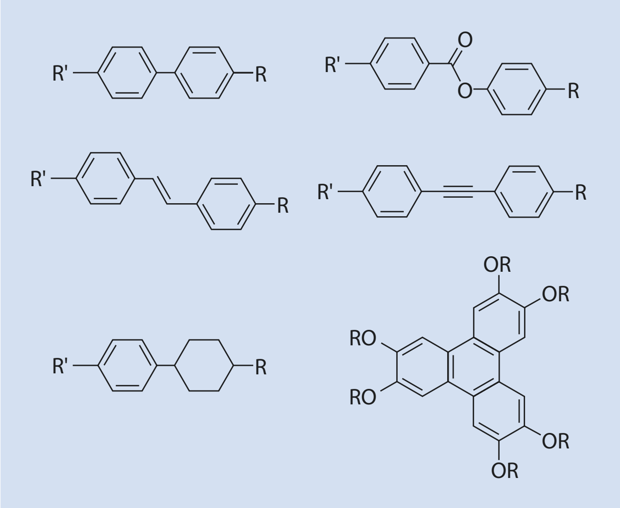


Fig. 20.3 Typical structural units in liquid crystalline substances

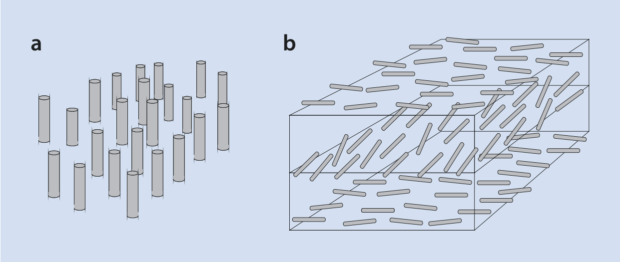


Fig. 20.4 Visualization of (**a**) nematic and (**b**) cholesteric phase (the rotation of one layer with respect to another by 90° is fortuitous)

The degree of orientation in relation to the direction field is a result of the thermal movement of the molecules. This value is designated by the *order parameter S*:

$$S = \frac{3}{2}\left(\cos^2 \Theta - \frac{1}{3}\right) \tag{20.1}$$

Θ is the deviation of the long axis of a molecule from the preferential direction. If all the molecules are oriented exactly in parallel, $S = 1$. For an isotropic melt, $S = 0$.

The cholesteric phase is closely related to the nematic phase. One can view the orientation shown in Fig. 20.4a as a level on which a vertical axis can be placed. If, along this axis, the preferential direction of orientation changes continually, the result is a nematic phase with a helical superstructure (cholesteric phase, Fig. 20.4b).

Cholesteric phases usually only occur in chiral mesogens or mixtures of achiral mesogens with optically active substances. This is why these phases are also called *chiral-nematic*. They are of great technical importance for appliances with displays.

The so-called smectic phases have a higher degree of order than nematic liquid crystals. In smectic phases the mesogens are ordered because of intermolecular interactions in equidistant lamellae, that is, with positional orientation (Fig. 20.5). At present a number of smectic phases are known which have been labeled from S_A to S_K depending on the date of their discovery. The individual phases can be distinguished by the orientation of the

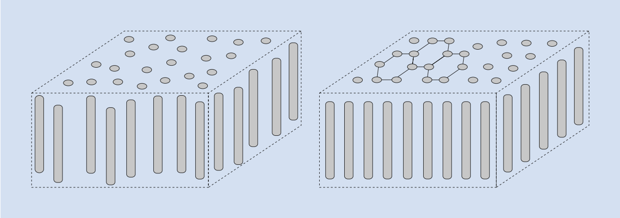


Fig. 20.5 Examples of smectic phases with varying degrees of order

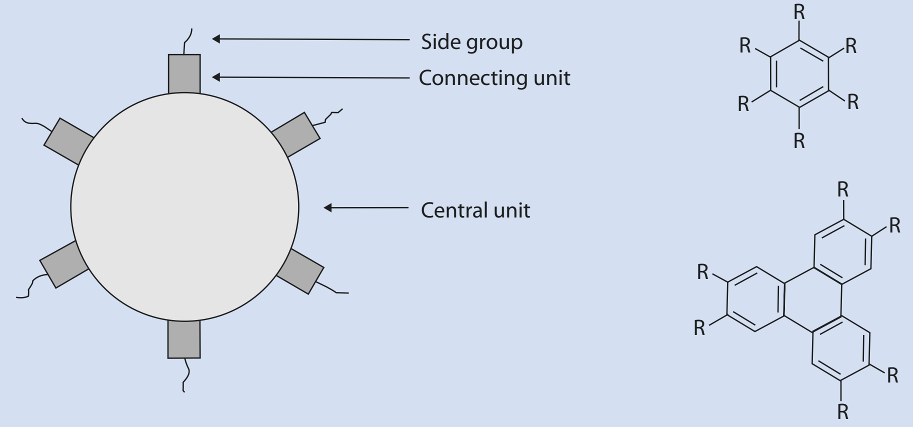


Fig. 20.6 Structural principle and examples of discotic mesogen with rigid central cores

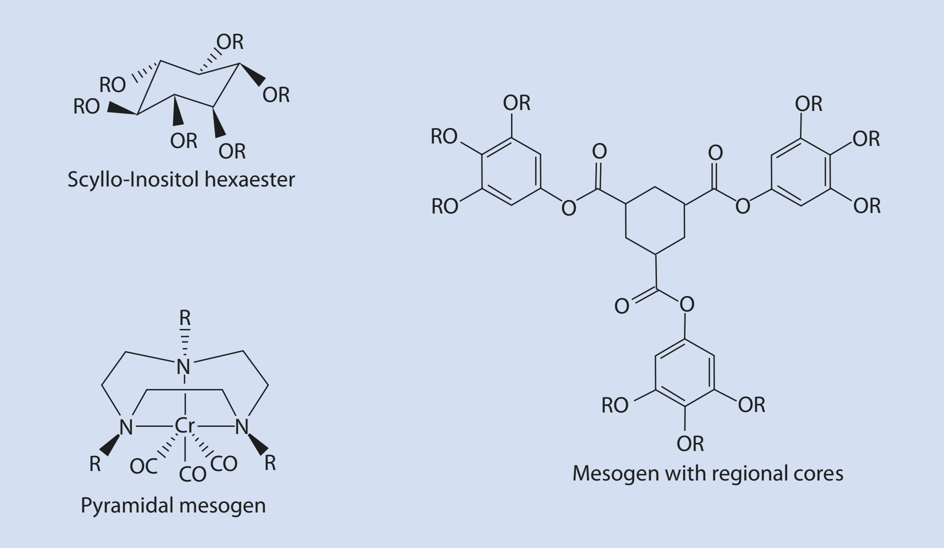
mesogens in each layer and the deviation of the director from a right angle to the layers. For more detail the interested reader is referred to the specialist literature.

In contrast to the situation in crystals, the individual layers in a smectic phase remain mobile with respect to one another. The viscosity of smectic phases is higher than that of nematic and cholesteric phases as a result of the higher degree of order.

So-called *polymorphic* mesogens pass through several mesophases when heated. As the temperature increases the phase with the highest energy (lowest order) is the most stable. Discotic mesophases can form from disc-shaped molecules. The general structural principle of this class of compounds is shown in Fig. 20.6. Discotic mesomorphism can occur if optimal area coverage is achieved by the side chains in the peripheral region and perfect space filling in the central area is achieved by the disc-shaped core of the mesogen.

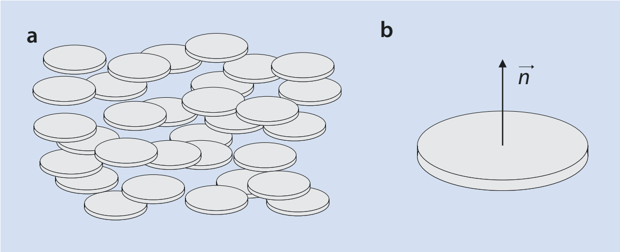
Classical discots are made up of a rigid, flat, disc-shaped central moiety onto which flexible side chains are attached via connecting groups. The central core can be an aromatic, heteroaromatic, or metal-complex system, onto which flexible side chains with ether, thioether, ester, or amide connecting groups are attached.

Scyllo-inositol hexaesters (Fig. 20.7) are examples of non-rigid central cores that form discotic mesophases. Mesogens with regional cores and pyramidal mesogens are also systems that deviate from the usual basic design of discotic mesogens. Their more ordered phases are thus better referred to as *columnar* or *stacked mesophases*.



◘ **Fig. 20.7** Examples of discotic mesogens without rigid, flat cores and without pronounced disc-like form

◘ **Fig. 20.8** Nematic-discotic mesophases. (**a**) Schematic diagram of the molecular order. (**b**) Orientation of the director



The nematic phase is also the least ordered phase in discotic systems. As in the calamatic-nematic phase the centers of gravity of the molecules are distributed isotropically in space and the mesogens have only a one-directional order. Although the director is parallel to the molecule's long axis in rod-shaped molecules, the preferential direction for discots is normal to the disc plane (◘ Fig. 20.8).

If discotic mesogens are stacked on top of one another, and thus form columns, then structures with two-dimensional order, such as hexagonal-columnar phases, are formed (◘ Fig. 20.9). The discotic molecules can have differing degrees of order along the column axis.

Some substances are able to form mesogens by association. This association can be caused by columbic-, dispersion-, van-der-Waals-, charge-transfer-, or hydrogen bond interactions. An example of this is shown in ◘ Fig. 20.10.

20.5 Characterization of Mesophases

A characterization of mesophases can be made using differential scanning calorimetry (DSC), polarization microscopy, and X-ray diffraction.

Fig. 20.9 Schematic diagram of a hexagonal columnar phase

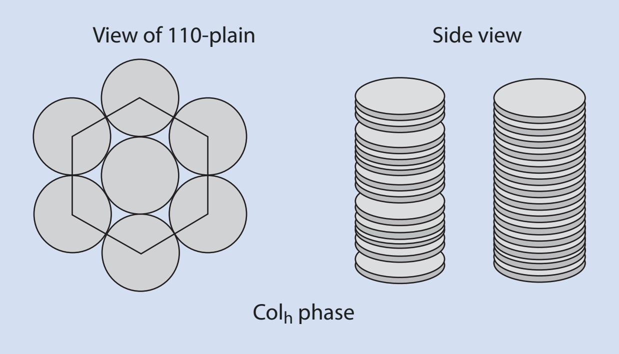
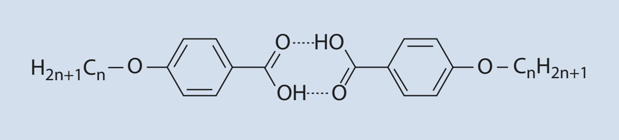


Fig. 20.10 Mesogenic cyclic dimer of a 4-alkoxy benzoic acid



20.5.1 Heat Flow Calorimetry

This method of DSC is one of the most important methods used in modern polymer analysis and in the analysis of mesophases for determining the thermal characteristics of new materials.

The temperature of the phase transitions and the associated enthalpy and entropy can be determined using DSC. With this method the first-order nature of the transitions between the crystalline, liquid crystalline, and disordered phases is exploited. Thus, the transition appears as a peak in the DSC thermograph, whose integral gives a measure of the heat associated with the transition. Figure 20.11 shows a typical thermograph with two transitions.

Such thermographs provide information about the temperature of the phase transitions and the degree of order. Highly-ordered phases generally exhibit strong hysteresis. In addition, the enthalpy of the transition increases with the difference in the degree of order across the transition (Table 20.1). The difference in temperature between the heating and the cooling cycle peaks for the same phase transition is caused by the relationship between the respective rates of phase transition.

20.5.2 Polarization Microscopy

Whereas DSC provides only indications of the existence of a mesophase, using a polarization microscope equipped with a thermostat-controlled stage enables one to determine exactly whether a mesophase is indeed present. A polarization microscope has a polarizer between the source of light and the condenser lens as well as an analyzer beneath the eyepiece. The sample can therefore be viewed in linear, polarized light. All (liquid) crystals that are not cubically symmetrical demonstrate birefringence.

When the light ray hits the coplanar birefringent sample it is split into two separate beams whose polarization planes are perpendicular to one another. These separate beams move in two different directions with different refractive indices and therefore have different speeds. This leads to a path difference when the light exits the sample, which is linearly

Fig. 20.11 DSC-curves of poly(8-(4′-methoxy biphenyl-4yl oxy)-octyl methacrylate) showing two phase transitions. (**a**) Heating. (**b**) Cooling

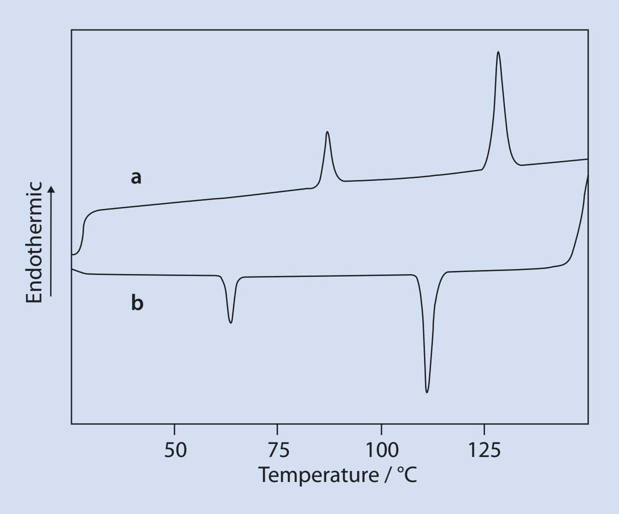


Table 20.1 Phase transition enthalpies (Kelker and Hatz 1980)

Nematic → isotropic	0.8–9.6 kJ/mol
Smectic → isotropic	2.9–12.9 kJ/mol
Crystalline → isotropic	7.0–117.0 kJ/mol

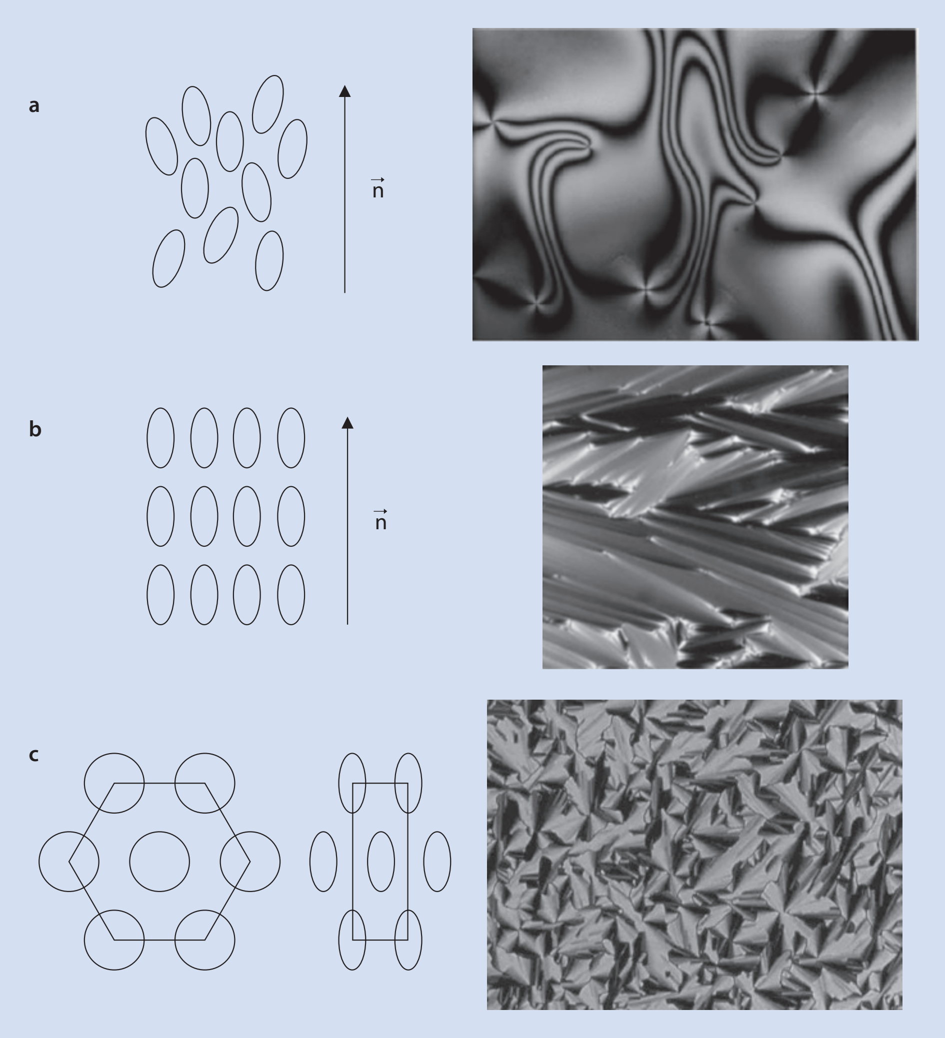
dependent on the thickness of the layer and the difference between the refractive indices. Because of this path difference, interferences occur, which result in a rotation of the oscillation plane of the light reaching the analyzer.

During the analysis, a thin layer of the sample is placed between two glass sheets. Subject to the arrangement of the mesogens in the different phases, characteristic defect structures are formed on the surface of the glass sheets when they come into contact with domains having different orientations, and when different domains come in contact with one another. The sum of these defects is referred to as texture. Examples of smectic, nematic, and cholesteric textures are shown in ◘ Fig. 20.12.

20.5.3 X-Ray Diffraction

X-ray diffraction is the most important method for characterizing the different mesophases in liquid crystals. The analysis of the position and intensity of the X-ray reflections allows an essentially complete description of the mesophase structure. Using monochromatic X-rays with a wavelength of λ, the direction of constructive interference of the beams diffracted by the structures with a periodicity d below the angle 2Θ can be determined using the Bragg equation:

$$n \cdot \lambda = 2 \cdot d_{hkl} \cdot \sin\left(\Theta_{hkl}\right) \tag{20.2}$$



■ **Fig. 20.12** Examples of (**a**) nematic, (**b**) smectic, and (**c**) cholesteric textures (Lavrentovich 2011)

A detailed discussion of the X-ray diffraction patterns of liquid crystals is rather complex and lengthy and is not given here.

Additional analytical methods for characterizing mesophases are miscibility studies with known liquid crystals, examination of the electro-optical behavior of mesophases, dielectric spectroscopy, atomic force microscopy (AFM), and rheology.

20.6 Liquid Crystal Polymers

A large number of structures are conceivable for polymers that have typical anisometric mesogen groups as repeating units (■ Fig. 20.13). In the first instance, one can distinguish between two basic types:

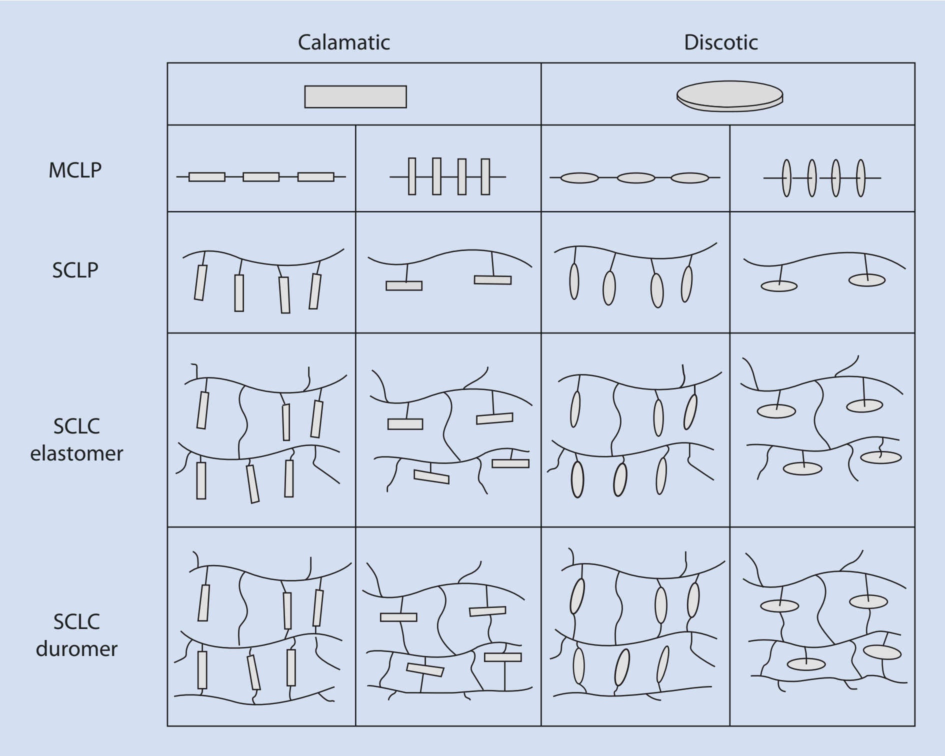


Fig. 20.13 Structures of polymeric liquid crystals. MCLP main chain liquid crystal polymers, SCLP side chain liquid crystal polymers

- Those with mesogen groups as part of the polymer main chain
- Those mesogen groups as part of the side chains

The subgroups MCLP (main chain liquid crystal polymers) and SCLP (side chain liquid crystal polymers) constitute the dendritic and highly branched liquid crystalline polymers described in ▶ Sect. 20.6.4.

20.6.1 Liquid Crystalline Main Chain Polymers

As can be seen in Fig. 20.13, anisometric mesogens are linearly or laterally connected with respect to their long axes. For this reason, rotations around the horizontal or vertical axes of the mesogens are inhibited. Most MCLP are linked linearly and the whole spectrum of reactions described in ▶ Chap. 8 can be used to synthesize them (Fig. 20.14).

However, the direct linking of mesogens often leads to problems, especially if, as a result of polymerization, the melting point changes and becomes higher than the decomposition temperature. A typical example is 4-hydroxybenzoic acid. Benzoic acid phenyl esters with low molecular weights are well-known liquid crystals. The analog polymer is, however, no longer fusible. The possibilities shown in Fig. 20.15 can be used to achieve a liquid crystalline state:

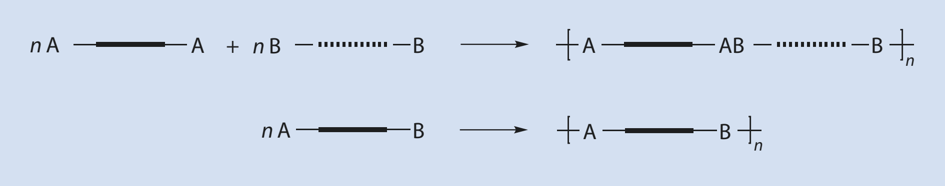
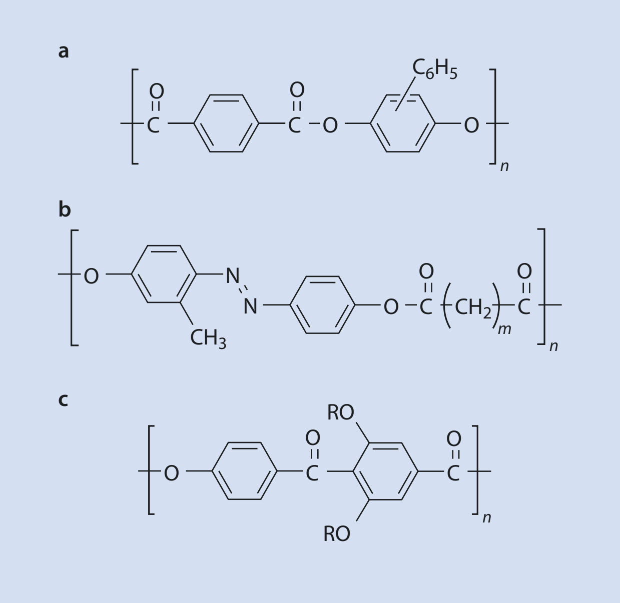


Fig. 20.14 Possibilities for combining monomeric mesogene to form MCLP

Fig. 20.15 Liquid crystalline polymers (**a**) with aromatic side groups, (**b**) with flexible main chain segments, and (**c**) with flexible side chains. R–$(CH_2)_nCH_3$



1. Comonomer building blocks with aromatic side groups are incorporated into the main chain (Fig. 20.15a)
2. Rigid mesogen groups are linked with one another using flexible spacers (Fig. 20.15b)
3. Flexible chains are laterally inserted into the mesogens as substituents in linear macromolecules (Fig. 20.15c)

Liquid crystalline main chain polymers often form nematic phases above their melting temperature. If a polymer is made up of two or more different monomer building blocks then smectic order is possible. The formation of the more highly ordered smectic phase is facilitated by the insertion of spacers between the liquid crystalline building blocks.

The melting point of rigid, rod-shaped polymers can be decreased by the addition of a suitable solvent to such an extent that a liquid crystalline state can be achieved. Thus, the aromatic polyamide shown in Fig. 20.16 can form a nematic phase in concentrated sulfuric acid.

Figure 20.17 shows an example of a lateral arrangement of a mesogen group in a main chain.

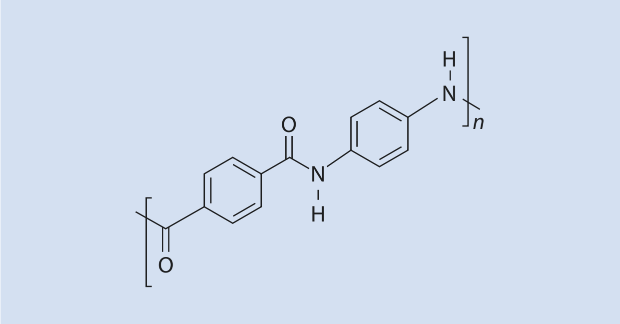


Fig. 20.16 Aromatic polyamide which forms a nematic phase in sulfuric acid

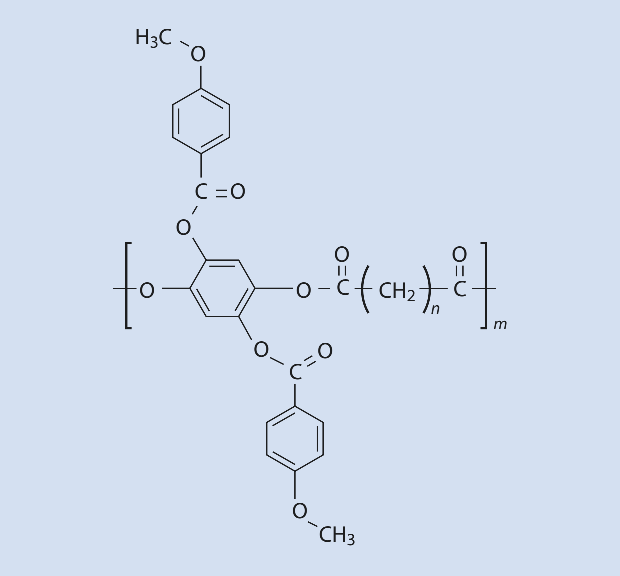


Fig. 20.17 Lateral arrangement of a mesogen group in the main chain. $n = 10$, 12, 14, 20

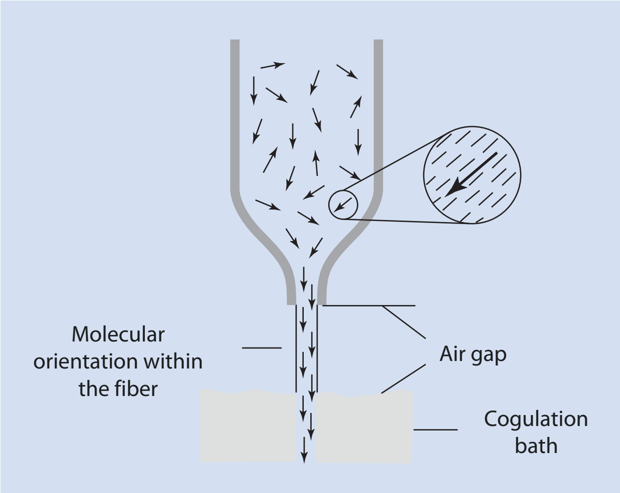
By spinning the polymers shown in Figs. 20.16 and 20.17 through a die, a macroscopically uniform orientation along the fiber can be imposed (Fig. 20.18). The ordered nematic structure is retained after cooling the fiber to a glass. The mechanical strength in the direction of the long axis is produced by the covalent bonds along this axis, and is thus very high, whereas horizontally van-der-Waals interactions, that is, significantly weaker forces, determine the tensile strength. Thus, polymers processed in this way are often used as high performance fibers.

Main chain polymers with liquid crystalline properties have gained industrial importance as fibers and in composite materials because of their exceptional mechanical properties, such as their high tensile strength after spinning, or their dimensional stability and low thermal expansion coefficients.

20.6.2 Liquid Crystalline Side Chain Polymers

The mesogen groups in SCLP are generally attached randomly along the polymer backbone by flexible spacers (Figs. 20.19 and 20.20). Radical polymerization and polymer analogous reactions are the most commonly used methods for synthesizing SCLP.

Fig. 20.18 Spinning an MCLP. → Director



In contrast to the analogous small molecule mesogens, the corresponding SCLP generally have lower transition temperatures and the liquid crystal phase transitions are dependent on the degree of polymerization; increasing with increasing degree of polymerization, usually, up to a degree of polymerization P_n of about 100.

The flexible linkage between the mesogens and the polymer backbone facilitates the formation of more highly ordered smectic structures if the side chain lengths are longer. The flexible spacer needs to be at least four atoms long. The rotation around the long axis of the spacer is only possible if the mesogen has a linear as opposed to a lateral arrangement.

If one cools LC- (liquid crystal-) polymers below the temperature at which liquid crystallinity first appears, phases with greater degrees of order can sometimes be obtained, just as for small molecular liquid crystals. However, the structure does not continue to change below the glass transition temperature of the polymer. This combination of glass state and anisotropic physical properties enables such polymers to be used as optical storage elements in the fields of linear and nonlinear optics. In modern electro-optical display elements, the position of the director is influenced by the application of external electrical or magnetic fields and its ordered state is then frozen by cooling the polymer to below its glass temperature.

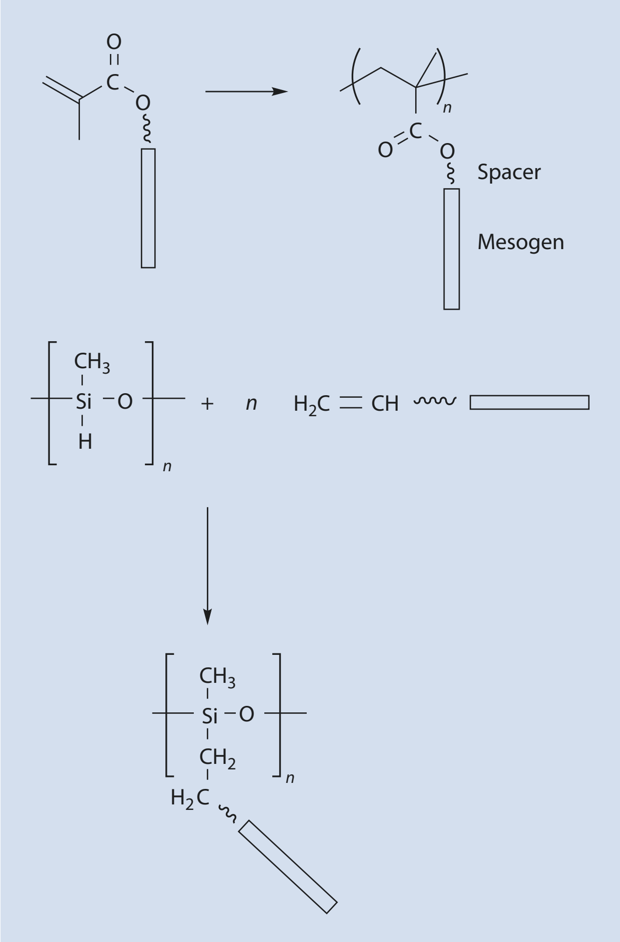
These materials can also be used for holography. An ordered polymer, which contains a dye exhibiting *cis*-*trans*-isomerism, can be heated by radiation and transformed into a liquid crystalline state. If isomerization of the linear *trans*-dye in the angled *cis*-dye takes place at the same time, then the state of order of the phase changes (▣ Fig. 20.21).

The disorder created by the laser beam is frozen by cooling the polymer to below the glass temperature. Thus, one can ‘inscribe’ something, such as an image, into a polymer layer.

20.6.3 Liquid Crystalline Elastomers (LCE)

If SCLP with flexible main chains are transformed into networks, the translational diffusion of the main chain is inhibited. However, the chain segments remain mobile. The movement of the mesogens linked to the network is less inhibited, and these can form liquid crystalline phases. Such systems display the behavior of small molecule liquid crystals and are dimensionally stable and rubber elastic, two typical properties of elastomers

Fig. 20.19 Synthetic route to SCLP



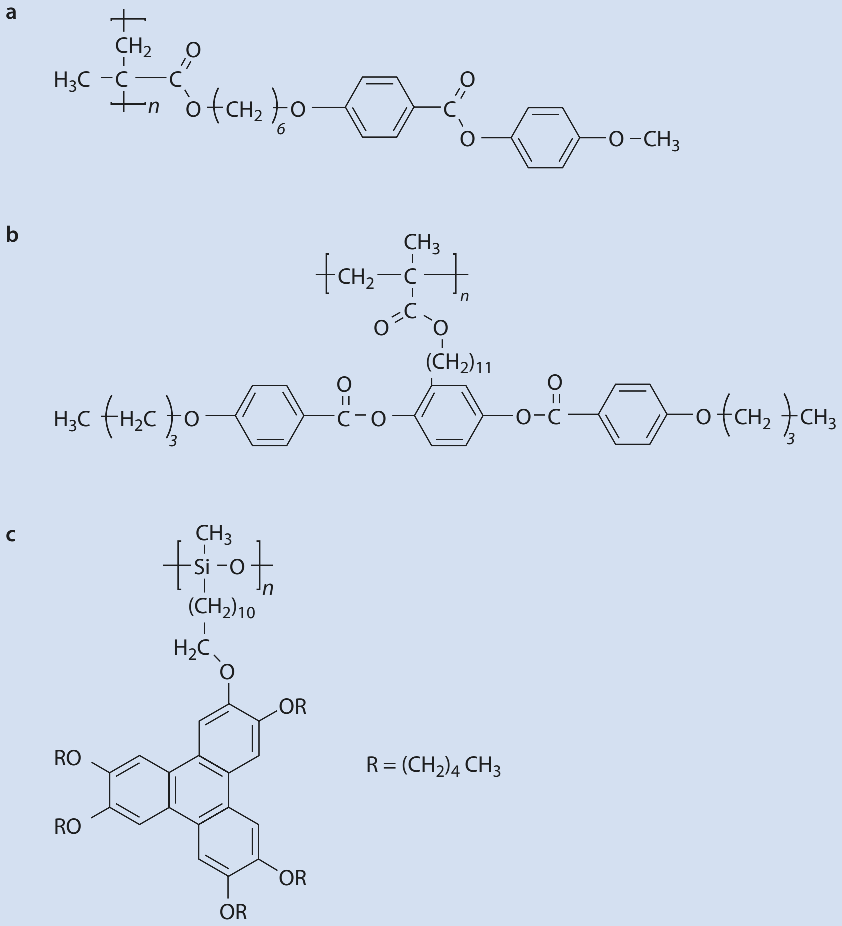
(▶ Sect. 18.8). The synthesis route shown in ◘ Fig. 20.22 has proved to be successful for these kinds of polymers.

It involves the copolymerization of mesogen monomers with monomers having an additional reactive functionality (A) that can be transformed into networks by reacting with B. Mechanical deformation of the rubber leads to a macroscopic orientation of the mesogens. These materials can be used, for example, as separating membranes.

A highly promising application of LCEs is as actuators. The incorporation of photochromic moieties into LCEs leads to materials which shrink when irradiated with UV light because of the photochemical reactions of the photochromic groups which can result in a decrease in the nematic order.

20.6.4 Dendritic and Hyper-Branched Polymers

Dendritic polymers can be distinguished from linear polymers by their multiple branches. These can be either structurally perfect with centrally-symmetric architectures (dendrimers) or star polymers without radial symmetry and randomly distributed



◘ **Fig. 20.20** Selected examples of SCLP. (**a**) Linearly bound calamitic mesogens. (**b**) Laterally bound calamitic mesogens. (**c**) Discotic mesogens

branches (hyper-branched polymers ▶ Sect. 8.3.3). Irrespective of structural differences, by linking mesogenic units to these branched structures, liquid crystalline phases can result.

As for linear LC-polymers, a distinction is made between those in which the mesogens are linked to the polymer structure via flexible alkyl units (◘ Fig. 20.23a) and those in which the mesogens form the terminal sections of the chains (◘ Fig. 20.23b).

Hyper-branched polymers are more easily synthesized than dendrimers. In spite of their less perfect architecture, they should thus be considered interesting alternatives to dendrimers as carriers of mesogens. Hyper-branched MCLPs were first reported in 1992

Fig. 20.21 Changing state of order because of laser irradiation

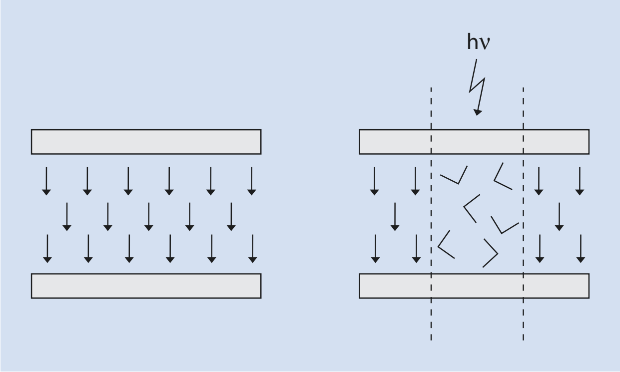
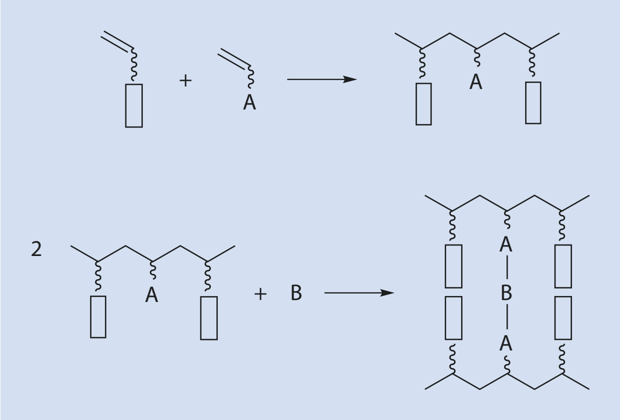


Fig. 20.22 Synthetic strategy for liquid crystalline networks (elastomers). *A* represents a reactive functionality, *B* represents a linking agent



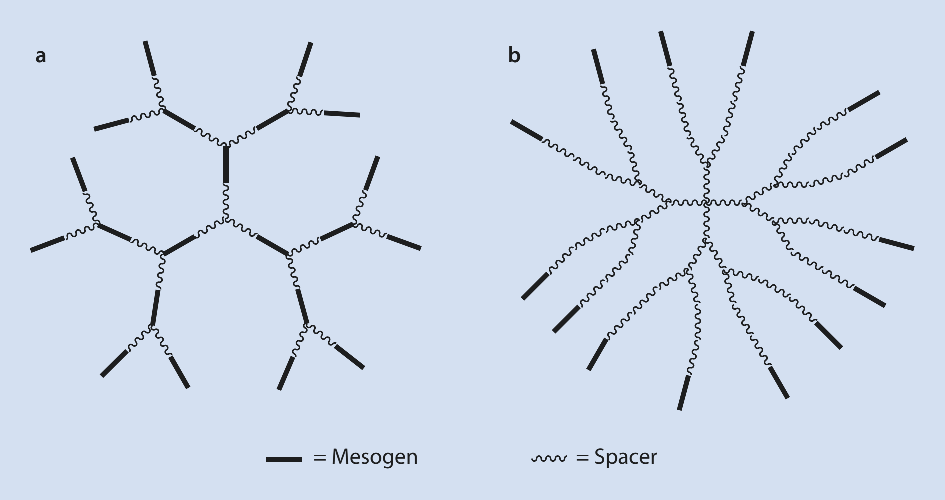
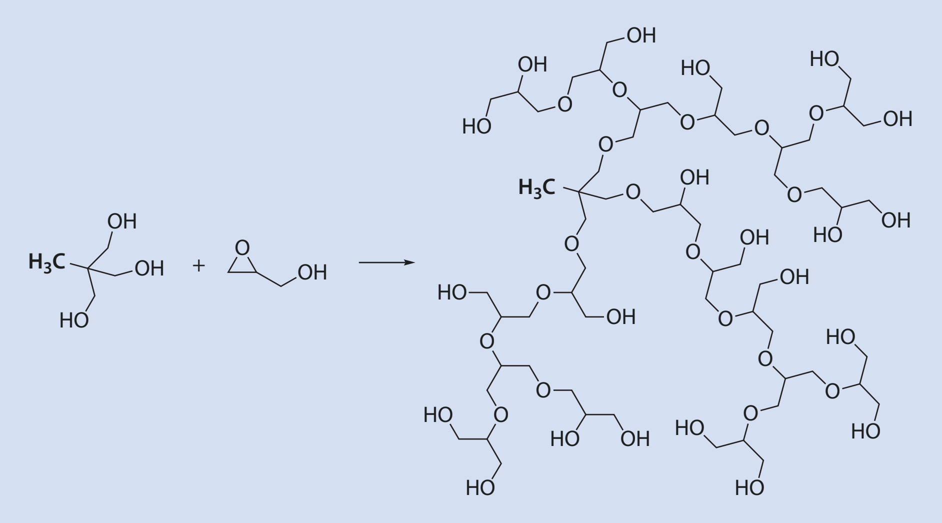
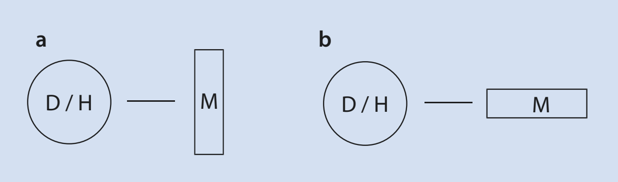


Fig. 20.23 Structures of dendritic LC-polymers. (**a**) Mesogens in the main chain. (**b**) Mesogens in the side chains



■ **Fig. 20.24** Synthesis of polyglycerine

■ **Fig. 20.25** Schematic visualization of (**a**) lateral and (**b**) terminal addition of mesogens to a dendrimer or a hyper-branched polymer. *M* Mesogen, *D* Dendrimer, *H* Hyper-branched polymer



(Percec and Kawasumi 1992). A suitable structure for end group functionalization with mesogens is the highly flexible and water-soluble polyglycerine (■ Fig. 20.24).

Thermotropic, hyper-branched LC-polymers can be obtained by functionalization with cyanobiphenyl (Sunder et al. 1999). The mesogens can either be linked laterally or at a terminal position to the dendritic or hyper-branched polymer (■ Fig. 20.25).

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