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LC-Polymers and Smectic Phases with Special Substructures/Nanophase Segregation

Rudolf Zentel

Liquid crystalline (LC) polymers find still a lot of interest, whereby the focus is—at present—on LC-elastomers with different phases and their application for mechanical actuation. While the LC-phases in LC-polymers can—generally—be well described in analogy to their low molar mass counterparts, some special properties became evident for some systems with smectic phases. They are related to the modulation of the nanophase segregation within the smectic layers and include often the formation of sublayers consisting of poorly compatible parts of the polymer like bulky (=non mesogenic) units, ionic groups, or poorly miscible parts of the main chain (e.g., polysiloxanes). Such a behavior can be found for semiflexible LC-main chain polymers and for LC-side chain polymers. Here the authors i) describe polymers for which such a modification of the smectic structure is observed, ii) discuss the origin of the deviation, and iii) describe possible application for the design of functional materials. The formation of the substructures can allow, for example, a mixing of the LC-polymers with other polymers, which have a good affinity to the second sublayer. It also allows it to separate, to some extent, the network structure from the packing of the mesogens in LC-polysiloxanes.

1. Introduction

This review deals with special modifications of smectic liquid crystalline (LC) phases, which are found in polymers and the resulting potential for LC materials. But first we start with LC-phases in a more general context.

Thermotropic LC phases are formed from molecules, which are shape- (or form-) anisotropic in a special temperature interval. The shape is thereby mostly rod-like and we will focus here on such "calamitic" liquid crystals (see **Figure 1**). For such molecules, which are called "mesogens" (=mesophase forming), the liquid-crystalline order is lost at high temperatures in the isotropic melt, which corresponds to a classical liquid. Upon cooling, the mesogens self-organize, however, in a certain temperature range (mesophase in between the classical liquid and the crystal) and adapt a long-range orientational order until the well-ordered crystalline phase is formed at lower temperatures. Thermotropic LC materials may exhibit several LC phases at different temperatures, which are distinguishable by the degree of order (Figure 1). The nematic phase is the least ordered mesophase and usually found at the highest temperatures. It is marked by an orientational order of the mesogens, meaning that their only alignment is along one common axis. Additional positional order of calamitic mesogens first appears at lower temperatures within layered smectic phases. In this case, the long axis of the mesogens aligns along the layer normal in a smectic A phase, while they are tilted to the layer normal in a smectic C phase. Additional smectic phases with an improved packing within the layers can exist at even lower temperatures. We will focus here on smectic phases, which possess a layered 1D density profile, layered substructure or nanophase separation.[1–3]

This layered structure of smectic phases is usually considered to be associated with a partial demixing of the core of the mesogens (mostly aromatic) and their side chains, which are mostly aliphatic.[1–3] However, because of the high mobility in smectics and the fact that they are LC-phases and "not-crystals," this demixing on the nanoscale can hardly be "stabilized" and used. It can, however, be modified by increasing the incompatibility of the different substructures of the mesogens, as it is, for example, done in lyotropic LC-phases.[4] It can also be modified by linking of the mesogens to a polymer chain and it can be stabilized in various ways by crosslinking, whereby the crosslinking requires the presence of polymer chains. The effect of crosslinks extends thereby from the creation of "some connectivity" perpendicular to the smectic layers to a dense crosslinking, which keeps the smectic layers intact, even in the presence of solvent. Examples for this will be discussed later in this paper.

Independent of the stabilizing effect of crosslinking (i.e., also in low molar mass liquid crystals), the nanophase separation can be improved and strongly modified by linking side chains with rather different solubility to the mesogens (aromatic,

R. Zentel
Department of Chemistry
Johannes Gutenberg University Mainz
Duesbergweg 10–14, D-55128 Mainz, Germany
E-mail: zentel@uni-mainz.de

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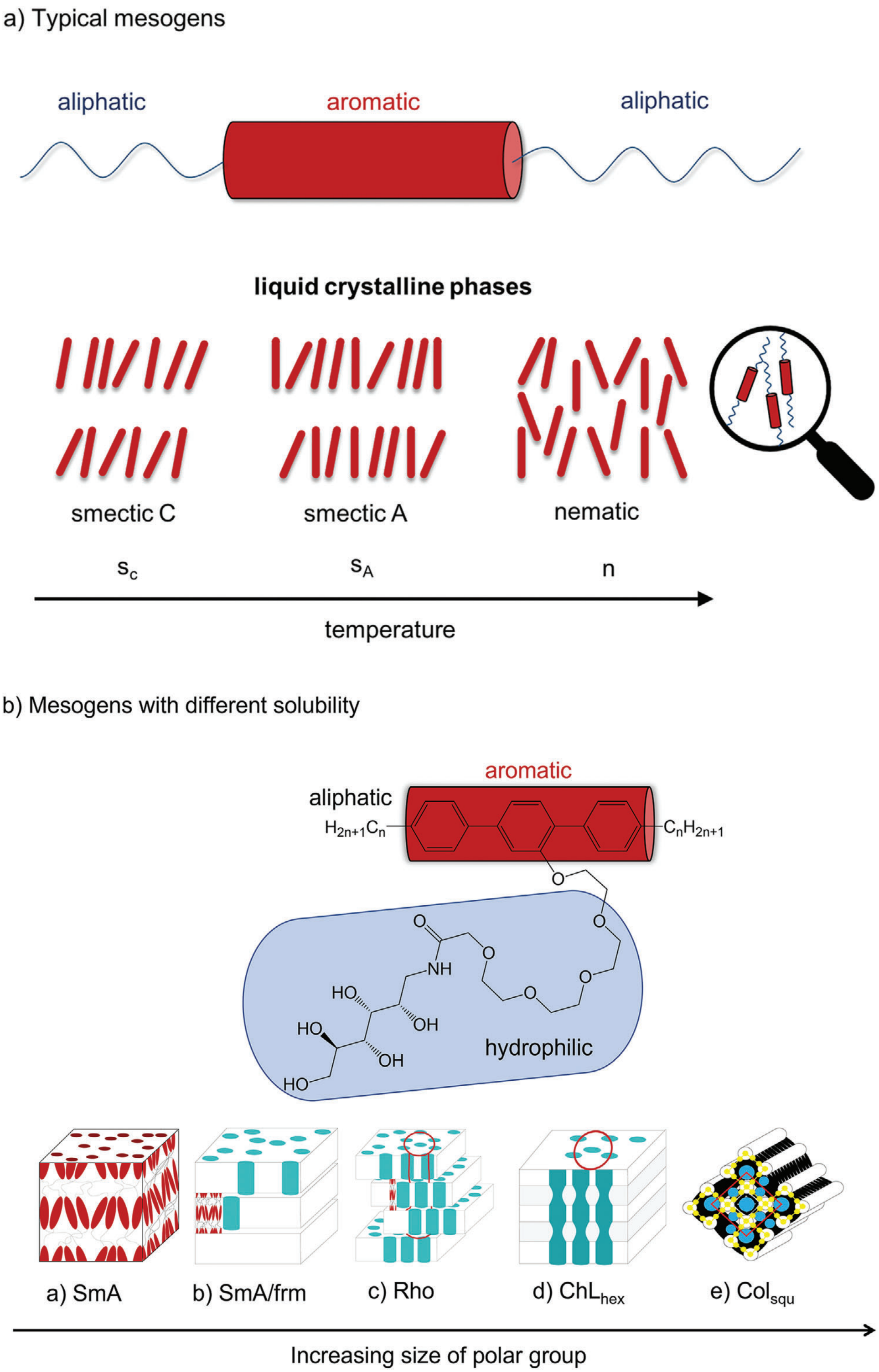

Figure 1. a) Thermotropic liquid crystalline phases (smectics and nematic) are formed—within a special temperature interval between crystalline and isotropic liquid phase (thus called mesophase)—from rod shape molecular structures, which are called mesogens. The mesogens consist thereby of an aromatic rigid core and flexible side groups, which are typically aliphatic. All smectic phases therefore possess some type of nano-phase segregation between aromatic and aliphatic substructures; b) the incorporation of a third molecular structure (here as side group), which is poorly compatible with the mesogenic core and the side groups leads to a broad spectrum of new phases with three different nano-compartments.[6–9]

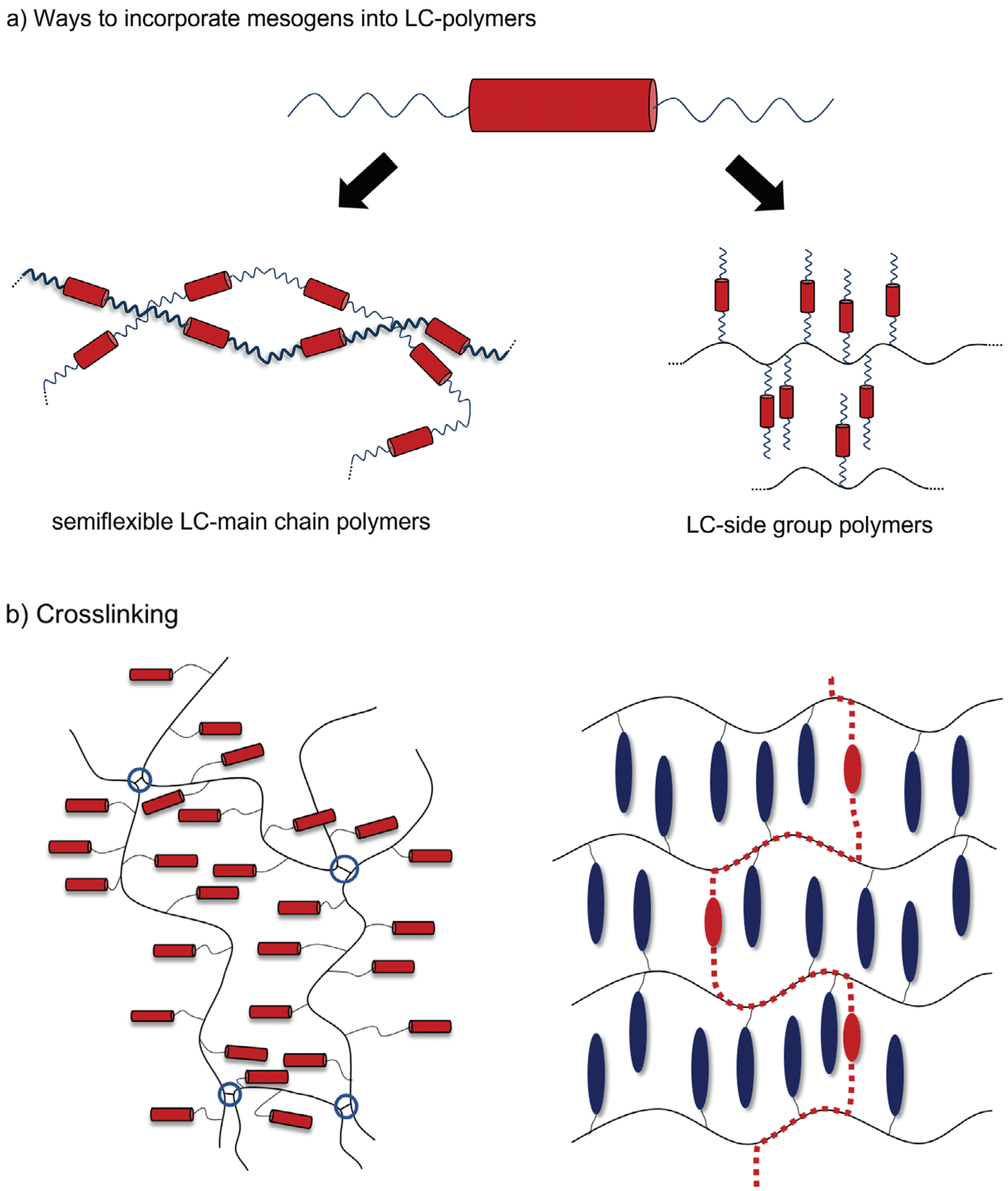

Figure 2. a) There are two different ways to incorporate mesogens in a polymer structure, either as LC-side group or as LC-main chain polymers; generally this creates some connectivity between the mesogens; note that the crossing of the spacers in the LC-main chain polymers is in the third dimension (no crosslinking). b) Crosslinking of the polymer chains is a very general way to create a long-distance connectivity between the mesogens via covalent bonds; its influence on smectic phases is especially strong because crosslinking couples mesogens located in different smectic layers (see Section 3).

aliphatic, perfluorinated, polyethylene glycole (PEG) containing, and highly polar subunits), because this stabilizes the tendency for nano-segregation in smectics.[4,5] Examples of this effect of nano-segregation in low molar mass liquid crystals on the phase formation have been studied intensively by Carsten Tschierske. It can lead also to very special LC-phases with three different types of nano-environments (see Figure 1b).[6–9] In this context especially "smectic" phases with a 3D periodic structure find a lot of interest because they can show an improved charge transport in three dimensions.[10,11] They are thus advantageous compared to discotic phases, which show a good charge transfer only in 1D (along the columnar axis).[12]

Considering the influence of the polymer fixation of mesogens, it is necessary to start with the different ways, in which the mesogenic groups can be incorporated into a polymer structure. This is done by linking them as side groups to the polymer backbone or by incorporating them into the polymer chain (see **Figure 2**).

2. Liquid Crystalline Polymers

Generally there are different ways to combine mesogenic groups and polymer structures, or to incorporate mesogenic groups onto polymers (see Figure 2).[13,14] Either the mesogens can be linked at both ends of the mesogenic tails to form a semiflexible main chain polymer or they can be linked at one end as side group to a flexible polymer (Figure 2a). Both structures can—in addition—be crosslinked (Figure 2b).

Linking of mesogens to a polymer creates some connectivity between them. This changes the LC phase transitions. At the same time flow processes in LC-polymers get dominated by the interaction of different polymer chains. So orientation by mechanical forces (e.g., stretching) becomes prominent. This effect is strongest for LC-main chain polymers and leads to the fact that the most popular use of these polymers is for the preparation of high tensile strength fibers. It is weaker for LC-side chain polymers, for which the focus has been more on the side of dynamic properties and reversible switching of the LC director in external fields. Crosslinking connects the different polymer chains further. It creates a 3D soft body (Figure 2b) including all polymers. It has been studied intensively for various LC polymers, which can be weakly crosslinked to form percolated elastomeric networks that still allow mobility on a molecular scale.[15–25] Such systems are called LC elastomers (LC-elastomers or LCEs) and there are various reviews on their physical properties and ways for their synthesis. They found since the time of their first observation—40 years ago—much interest because of the coupling of the order of (different) LC-phases with the rubber elasticity of a polymer network. They are recently still a hot topic in liquid crystal research, because LCEs give good mechanical actuators, which deform reversibly by temperature change, irradiation with light or the application of strong external electric fields. This makes them interesting for micromachines and the field of micro-electric-mechanical-systems. Now, during the last years, research on LCEs adopted a strongly applied (engineering) aspect, focusing on simple synthetic routs and processing steps to make LCEs and combining it with routs to control the LC director alignment in directly made LC microparticles and objects. So synthetic work focuses on the use of bisacrylated (commercially available) mesogens in combination with bisthiols, which are processed by a combination of Michael-addition of the thiol and radical polymerization of the acrylates.[26–29] In addition elastomers with exchangeable bonds are often used, because they facilitate the control of the director alignment.[30,31] As most of the actuators will be used in an open environment, many studies focus directly on the preparation of LCE-particles or objects. For this purpose microfluidic and spinning processes are often applied.[32–35] In this context ways to produce directly more complex actuator structures or to include magnetic nanoparticles for macroscopic guiding are studied.[36,37]

To induce the shape change of the LCE actuators directly, electrically heatable LCEs with temperature feedback are under investigation.[38–40] In addition, illumination to induce the shape change is often applied.[41–44] Topics are here to induce bending or to avoid it (homogeneous shrinking) and the use of visible light.[41–43,45]

As most of these topics focus on the preparation of a complex system, the LCEs possess usually just a nematic phase. However, there is a lot of fascinating properties of smectic systems, including their ferroelectricity (see below), which might be—out of focus today—but which has potential for future applications.[46,47] And it is always rewarding to search for a deeper understanding of the underlying physics.

Thus, this review will summarize different aspects of the influence of polymer fixation on smectic phases.

3. Liquid Crystalline Polymers and the Influence of Crosslinking on Smectic Phases

Crosslinking of LC-polymers and thereby crosslinking of mesogens can influence the structure of smectic phases also in a very general way. And this requires only a very light crosslinking; just enough to create a soft solid (an elastomer). That is because crosslinking leads to smectic phases, which are 3D soft solids on a macroscopic scale (see Figure 2b). And this leads to a long-range correlation between the layered structure of the smectic phase, while in smectics formed by low molar mass liquid crystals there is only a 1D density correlation of the mesogens. And because of this low-dimensionality (i.e., only a 1D periodic layered structure) the translational order of the smectic layers gets partially destroyed through the "Landau–Peierls instability." As result the amplitude of the displacement from the perfect periodic order increases with the size of the system.[1,48–50] This effect is known for various layered systems ordered in only one dimension, such as surfactant membranes, smectic (layered) liquid crystals and also LC polymers.[51–53] Thus, classical smectics (smectics from low molar mass liquid crystals) do not have a "true long-range order" in contrast to ordinary 3D crystals, which are characterized by long-range translational order in all three dimensions.

Linking the mesogens to polymer chains as in LC-polymers offer here different ways to modify the interaction between mesogens through-bond and various consequences of it will be discussed here.

The most general possibility—in this context—is crosslinking, which creates a 3D soft body (Figure 2b). It has been studied for smectic LC polymers, which can be weakly crosslinked to form percolated elastomeric networks that still allow mobility on a molecular scale.[15–17] In these smectic elastomers, fluctuations of the fluid layers are, however, coupled to distortions of the underlying network, and are therefore energetically penalized, even though the network of crosslinks has a random nature and thus no 3D translational order.[54] Thus the introduction of a random network of crosslinks can enhance the stability of the layered structure against thermal fluctuations, suppress the "Landau–Peierls instability" and induce so a "1D" long-range ordering at length-scales up to several micrometers.[55,56]

The influence of the crosslinking on the order in smectic phases, is, however, still more complex (see Figure 2b). From a chemical point, all netpoints are defects in the perfect smectic structure (or a mixed-in different structure/impurity). Thus, they tend also to destabilize the smectic layer structure. And this effect increases with the crosslinking density as studied in detail for a series of polysiloxanes.[57,58] Thereby it turned out that a crosslinking density of 2,5 mol% (2,5 crosslinks per 100 repeating units) improves the smectic order by creating a 3D connectivity of the polymer chains, about 5 mol% show no significant effect, while 10% lead to a weakening or partial destruction of the smectic layering (the absolute crosslinking necessary for this will depend on the exact structure of the netpoints). From a pragmatical point of view, the stabilization or destabilization of the smectic structure by crosslinking will thus also depend on the

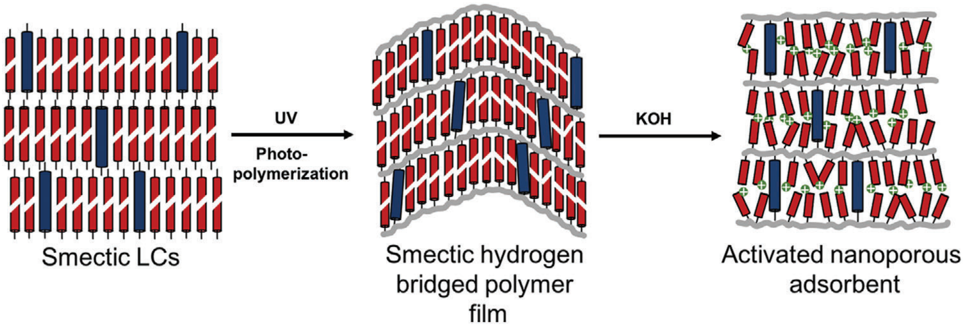

Figure 3. A dense crosslinking of smectic phases composed of mesogens, which are dimers of carbonic acid dimers (red structures), leads to smectic materials with ionic pores in the nm-range.[69]

molecular weight of the polymers to be crosslinked and therefore also on the way they are prepared and on their structure. LC-polymethacrylates and polyacrylates can easily be prepared with a high molecular weight.[17] They require thus only small amounts of crosslinks to obtain well crosslinked LC-elastomers.[17] These are the systems for which the stabilization is mostly observed.[55] LC-polysiloxanes, on the contrary, are made by reactions on a preformed polymer.[16,59–65] Since the reactive polysiloxane precursors possess usually a lower molecular weight, the necessary crosslinking densities are here higher and a destabilization of the smectic layering is more often observed.[57,58]

At last, there are some fascinating aspects for an application. A really dense crosslinking leads to a hard material, which loses the possibility for phase transitions. As discussed at the beginning, the crosslinking process might weaken the long rang order in smectic materials, but it will not destroy the smectic short-range order. But crosslinking will inscribe the smectic short-range order in the thermoset. Thereafter it can withstand hard conditions like various solvents (a thermoset is no longer soluble) and high temperatures. Thus, crosslinking is a way to prepare well-ordered nano-porous membranes with a smectic order.[66–68]

A dense photo-crosslinking of monomers with a smectic phase leads to stable smectic films, whose structure survives even harsh conditions. If the smectic layers contain mesogens from hydrogen bonded acids, ionic structures can be incorporated into the smectic structure and this leads to pores with a 2D geometry, which can be used for separation purposes (see **Figure 3**).[69,70]

In this context previously a fabrication process for nanoporous membranes based on the self-organization of reactive thermotropic hydrogen-bonded smectic liquidcrystals (LCs) has been reported.[71,72] The membranes were created by photopolymerization to lock the smectic structure into a network followed by an alkaline treatment to break the hydrogen bonds. In this way minute interstices are formed and the smectic nature of the material results in pores with a 2D geometry. These pores could be filled with silver ions, which could be reduced to silver nanoparticles.[73] In this way an efficient and selective porous nanostructured polymer adsorbent is prepared from smectic liquid crystals.[69] The anionic pore interior of the nanoporous polymer is able to selectively adsorb cationic model compounds over their anionic pendants and the confined pore dimensions allow size selective size discrimination in adsorption; a 4th generation cationic dendrimer is not able to diffuse into the nanometer sized pores. On the other side the porous nature of the polymer provides easy and fast accessibility of all adsorption sites and a stoichiometric ion exchange is obtained.[69]

Now, besides the very general possibility to modify the smectic phase in elastomeric materials by crosslinks, who might either strengthen 3D long-range connectivity or act simply as defects, a connection of the mesogens to polymer chains offers already many additional possibilities to modify smectic phases by introducing different structures inducing bended conformations or a repeated demixing of different partial structures. Generally this leads to "special substructures/nanophase separation" which are not found in low molar mass liquid crystals and have some similarity to the polyphilic liquid crystals introduced by Tschierske.[6–9] This discussion will be done following the different ways, in which the mesogenic groups can be incorporated into a polymer structure, which is by linking them as side groups or by incorporating them into the polymer chain.

4. Smectic Main Chain Polymers with Special Side Chains

Semiflexible main chain polymers consist of mesogenic groups, which are linked at both ends to create a polymer. They form various types of LC phases in quiet analogy to low molar mass liquid phases.[13,14] And as the tails of the mesogens consist usually of alkyl-chains the rigid cores of the mesogens are mostly connected by alkyl spacers.[13] For such systems it has been proven that the flexible spacer adopts a straight conformation in the LC-phase.[13,74] So they form a structure as presented in Figure 2a in the LC phase with a straight (elongated) spacer, preferably in all trans conformation in the LC-phase.[13,74] This has been proven for nematic polymers with *n*-alkyl chains as spacer.[13,74]

For polymers with different spacer chemistry, for example, spacers consisting of ethylenoxide or substituted malonic esters there is, however, no evidence for such a straight conformation (**Figure 4**).[13] This is probably the result of the fact that there is no preference for an "all trans" conformation around the O–C bond.[75] This effect becomes very prominent in smectic polymers with bulky more complex structure in spacer like phenylmalonate units. For them a repeated bending of the main chain spacer between the mesogens (not straight spacer) is observed (Figure 4).[76–82]

This regularly bended structure allows now the incorporation of functional, even sterically demanding units as side groups, without disturbing the dense packing of the mesogens and thus

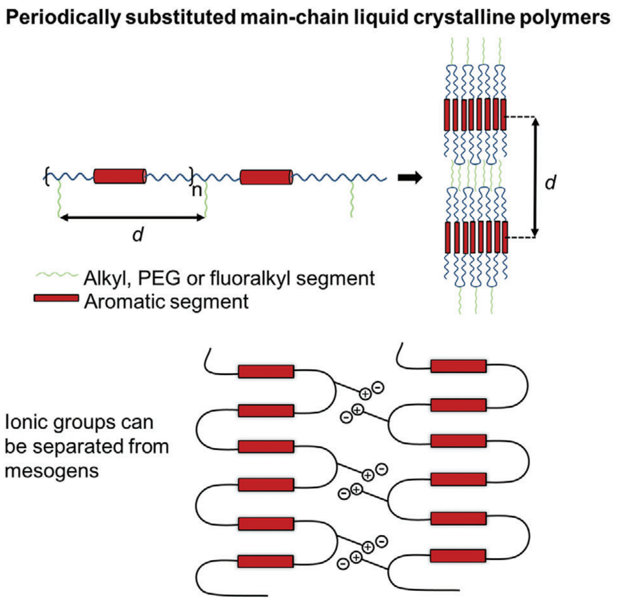

Figure 4. The spacer in semiflexible LC-main chain polymers tends to fold, if it is periodically substituted.[77,82] This leads to a separation between mesogenic core, the unsubstituted part of the spacer (typically alkyl-chains) and the units used as substituent (ranging in size from phenyl to rather bulky (also ionic) groups).

without disturbing the LC ordering.[76–82] Concerning the smectic structure the smectic layer thickness includes the length of the side chains (Figure 4). In smectic elastomers prepared from these systems, the shape variation at the phase transition to the isotropic phase is well detectable, but much lower than in the case of LC-main chain elastomers with a straight spacer.[83] This is a natural consequence of the less extended conformation of the polymer backbone in the direction of the LC director.

A special class of these semiflexible smectic main polymers is “combined” LC main chain/side chain polymers, which contain mesogenic groups both in the main chain and as side groups. These “combined” LC main chain/side chain polymers are reviewed in ref. [84] in detail. Also in their case the spacer is bending between the main chain mesogens and—as result—the smectic layer thickness is determined by the length of the main chain mesogens and the length of the side chain mesogens.[84] Thus, with regard to their smectic structure they follow the rule for main chain polymers substituted with bulky groups in the spacer.

The regularly bended structure and the underlying demixing gets especially strong if ionic groups are included in the spacer.[76,77,85,86] The systems can combine thus concepts of a lyotropic phase (demixing of hydrophobic and hydrophilic part) with classical thermotropic LC-phases (parallel orientation of the mesogens). Systems which are both thermotropic and lyotropic are called amphotropic (see **Figure 5**).[76,77,85,86] Such LC-polymers with ionic side groups can be used for a reversible crosslinking of LC-polymers by the formation of ionic clusters in the apolar LC-phase.[87,88] Alternatively it can be used to build multilayer structure with other polymers by “layer-by-layer” assembly (Figure 5a).[85,86] Finally it allows the formation of very thin polymeric multilayers, whose thickness is a result of the number of the individual sublayer.[78,79] Such thin layers are discussed in more detail for side chain LC polymers below (Section 5.1 below).

5. LC-Side Chain Polymers with Statistically Incorporated Non Miscible Units

In this section we will discuss LC side chain polymers (mesogens as side groups, see Figure 2) into which not mesogenic molecular structures are statistically introduced. Most important is thereby that these molecular structures are not miscible with the mesogens. They can be ionic side groups (side chain LC-ionomers, Section 5.1) or unmodified but purely miscible parts of the main chain as in the diluted LC-polysiloxanes (dimethyl-siloxane units, Section 5.2). This induces some internal demixing in different sublayers and this modifies especially the stability and the properties of smectic phases. As there is not much order of the polymer chain in LC-side chain polymers (in fact it is close to a random coil) no information on chain bending is available. However, some information about global change of conformation as result of demixing can be obtained.

5.1. Side Chain LC-Ionomers

In the case of side chain LC-ionomers 10 to up to 50 mol% of ionic groups are introduced. They are not miscible with the hydrophobic mesogens. Thus, some local demixing between mesogens and ionic groups occurs, which leads—at low concentration—to the formation of ionic clusters in the more hydrophobic matrix.[87] These ionic clusters can act as reversible netpoints to crosslink the material.[87,88] In addition they can be used to disperse the LC-ionomers in other types of non-LC polymers. So finely dispersed composites from LC and non-LC polymers can be obtained. These properties do, however not depend on the type of LC-phase present and can be applied to nematic and smectic systems.

For LC-side group polymers with a higher amount of ionic groups (about 50%) a demixing similar to the situation in lyotropic LC can result (see Figure 5b).[89] This stabilizes smectic phases. For some of these polymers amphotopic LC-phases can be observed, which are thermotropic (neat compound) and lyotropic at the same time.[89]

These results in a situation similar to the main chain polymers discussed above (Section 2) and it gets also possible to build multilayer structures with other polymers by “layer-by-layer” assembly. For this purpose, thin layers of oppositely charged polymers (cationic polymers with low molar mass anionic counterions and vice versa) are sequentially adsorbed on a substrate from solution.[86,89] Thereby molecularly thin layers of the two different polymers are formed in the structure of a multilayer stack (see Figure 5).

So the introduction of ionic groups, which are immiscible with the mesogenic matrix leads both in main chain and side chain LC-polymers to similar properties. The resulting smectic structures possess two different milieus on the nanometer distance, a situation, which is similar to lyotropic LC-phases. In addition,

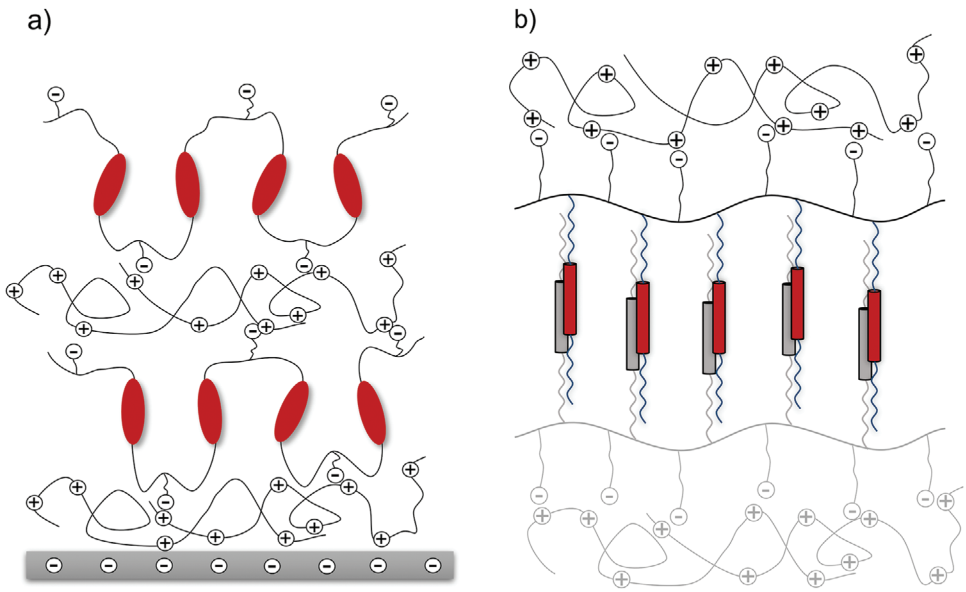

Figure 5. a) Main chain LC-polymers functionalized with ionic groups in the spacer can be processed into multilayer structures with amorphous polymers of opposite charge.[85,86] b) LC-side group polymers with ionic groups can form amphotropic LC-phases, which resemble also lyotropic structures, as the polar ionic groups and the hydrophobic mesogens are separated into sublayers.[89] Such structures can also be processed into multilayers.

the ionic groups can be used for a reversible crosslinking due to the formation of ionic clusters and they can be used to disperse different, oppositely charged polymers, that is, to prepare composites from LC and non-LC materials.[87,88]

5.2. LC-Polymers from "Diluted" Polysiloxanes

It is most easy to introduce LC-polymers from "diluted" polysiloxanes by putting them into the framework of liquid crystals and their interaction with electric fields. That is because the switching of low molar mass liquid crystals in electric fields is the property, which makes LC-displays the dominant type of displays.[14,90] And side chain LC-polymers were studied from the beginning also to mimic the switching of low molar mass liquid crystals.[91]

Now the first LC-side chain polymers were synthesized with a polymethacrylate backbone, but this led to higher glass transition temperatures, which limit their dynamic at room temperature and make switching only above 100 °C possible. To reduce the glass transition temperature, the polymer backbone was changed from polyacrylates to polysiloxanes in the attempt to reduce the glass transition temperature as the lower temperature for operation.[91] This work is reviewed in ref. [92]. From there on a lot of work focused on LC-side group polymers with a polysiloxane backbone.

The work on LC-polysiloxanes started with homopolymers but extended later on to copolymers, in which only a part of the dimethyl-siloxane units on the polymer chain are substituted with mesogens (so many dimethyl-siloxane units, which are poorly compatible with the mesogens, are present in the polymer backbone).[59–65,92–96] This was done to decrease the glass transition as far as possible below room temperature and—in fact—LC phases in the region around room temperature could be achieved.[62,92] Thereby it was recognized that these copolymers—the so called "diluted" polysiloxanes—were still LC despite the low amounts of mesogens. This observation is different from that on LC-polyacrylates, which loose liquid crystallinity at much lower amounts of non-mesogenic repeating units along the polymer chain.[97] In polymers with paired mesogens, in which the mesogens can be especially strongly diluted with dimethyl-siloxane units, a first observation of nanophase-separation was made then.[65]

Now, copolymers derived from usual LC side group polymers by incorporation of non-mesogenic groups of different natures have been studied by different authors.[62,97] The main conclusion drawn from these studies is, that the incorporation of non-mesogenic units to the extent of more than 50% in relation to the total number of chain segments hinders the mesophase formation progressively. For polymers with paired mesogens, however the width of the LC phase is retained up to high contents (e.g. 90%) of non-mesogenic units.

Further work on copolymers was associated with systems for electro-optical applications and focused mostly on ferroelectric liquid crystals and their switching.[5,98–101] Due to their structure it was possible to reduce the minimal temperature for switching down to room temperature, while it was high for the polyacrylates or even polymethacrylates.[5,100,102]

On the other side, much of the work on general materials properties of LC-polymers focused on polysiloxane homopolymers.[93,94]

Now the special property of the "diluted" polysiloxanes, in which only a part of the repeating siloxane units are functionalized with mesogens (down to 1/4), is the fact that the glass transition temperature can be lowered by incorporating many unfunctionalized dimethylsiloxane units, while preserving the smectic phase. This differentiates them from LC-polyacrylates, which lose their liquid crystallinity, if more than 30% of unfunctionalized repeating units are present. The fact, that this is due to

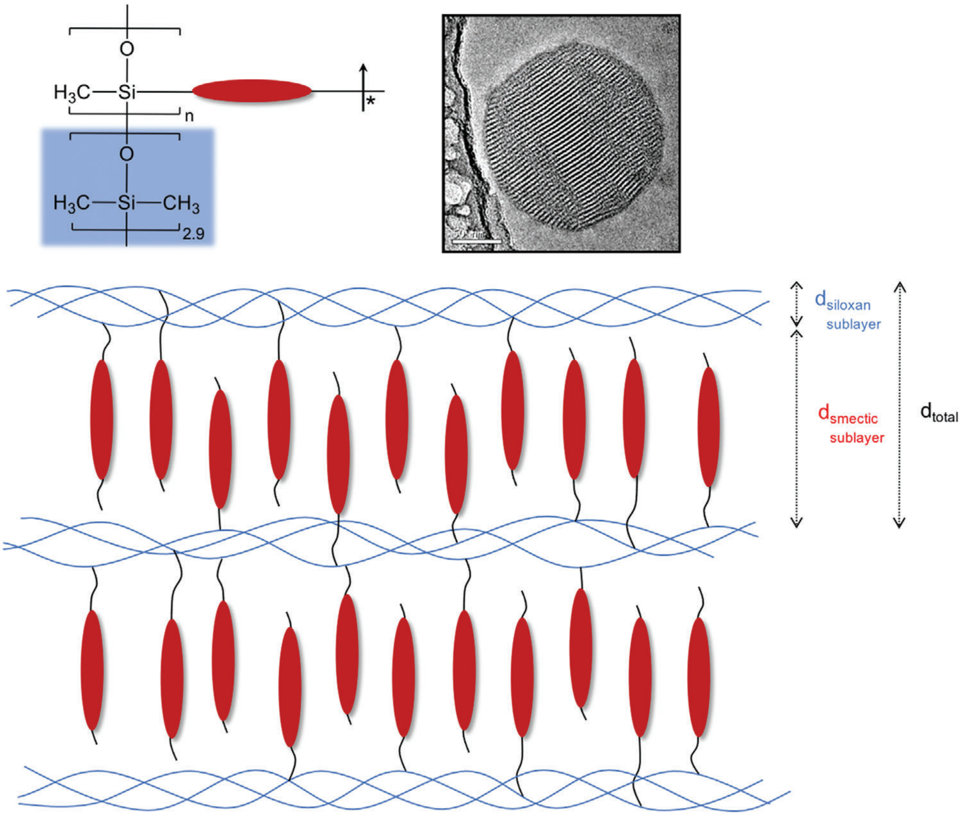

Figure 6. "Diluted" polysiloxanes demix in their smectic phases into sublayers of mesogens and unfunctionalized poly-dimethylsiloxane units.[65,100] This nanophase separation can be directly visualized by transmission electron microscopy (TEM).[103]

a demixing of the nanoscale, was recognized rather early.[65] The proposed smectic structure is presented in **Figure 6**.

Out of this structure the following specialities of the "diluted" polysiloxanes follow:

- "Diluted" LC-polysiloxanes show nearly exclusively smectic (layered) phases and only in very rare cases nematic phases.[62–65]
- In analogy to the LC-ionomers the smectic layer thickness includes the nanophase separated siloxane layer. It increases thus with the amount of unfunctionalized siloxane units.[65]
- It gets possible to mix in oligosiloxanes (not chemically bound) and still have a homogeneous smectic phase.[65] This leads to an additional increase of the smectic layer thickness (please note that, this does not work for high molar mass polydimethylsiloxane (PDMS). Obviously, the entropy penalty to compress the PDMS coil into a 2D layer gets too big in this case. As a result, the two components demix and the system becomes two phasic).
- Oligomers (dimers) in which two mesogens are just linked by a siloxane spacer become very comparable to polymers.[5,101]
- While low molar mass smectics show mostly only one order of reflection for the smectic layers in X-ray measurements (this corresponds to a sinusoidal density profile), diluted LC-polysiloxanes show many higher orders of the smectic layer reflection.[100,104,105]
- In some cases, smectic layer reflections can be observed for up to 10 °C above the LC-phase in the isotropic phase.[105] This is an indication of some remaining microphase separation between mesogens and dimethylsiloxane units, still present after the mesogens have lost their orientational correlation at the clearing point. A slight crosslinking, which stabilized the microphase separation, shifts the disappearance of the small angel reflections up to 50 °C into the isotropic phase.[105] So there is some decoupling of the melting of the mesogens in the smectic layer (loss of their orientation) and the complete demixing between mesogens and PDMS sublayers. These effects are, however, not found for the polysiloxane homopolymers, which show no sign for nanophase separation.[105]
- In addition, the demixing is so strong that the sublayers of mesogens and siloxanes can be visualized directly by TEM measurements of the "diluted" LC polxsiloxanes (see Figure 6).[103]

This formation of a siloxane sublayer parallel to the smectic layers is essential for the ferroelectric switching in tilted chiral smectic C* phases. The ferroelectricity of chiral smectic C* phases is a result of their low symmetry (tilted smectic phase made of chiral molecules) and this low symmetry (no mirror planes) leads to a macroscopic electric polarization, which is oriented perpendicular to the normal of the smectic layers and perpendicular to the tilt direction (**Figure 7**).[106] Because of this symmetry the switching happens by a rotation of the

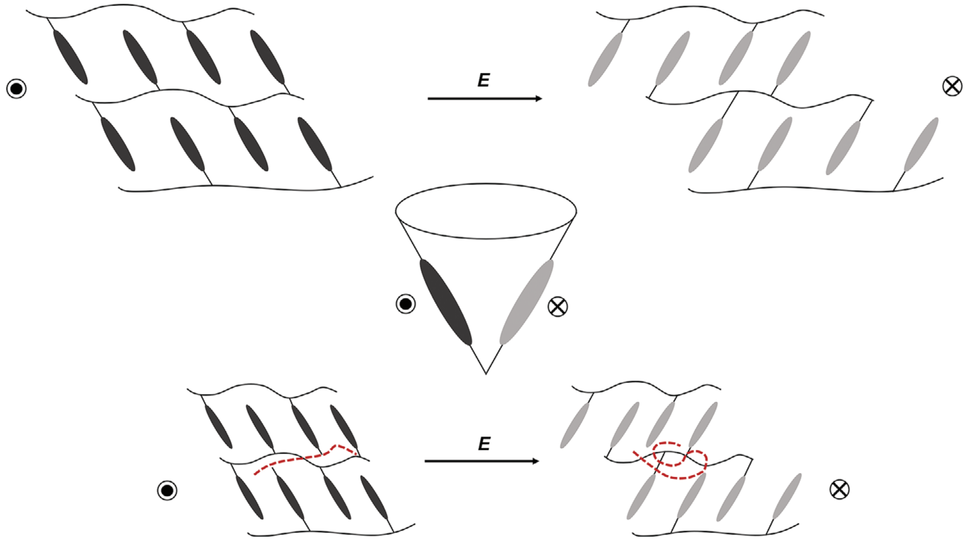

Figure 7. The ferroelectric switching in LC-polysiloxanes (upper line) with a chiral smectic C* phase relies on the fact that there is a permanent electric polarization per layer of the tilted mesogens.[98–100] It is oriented perpendicular to the layer normal and perpendicular to the tilt direction. The inversionof the sign of an external electric field lets the mesogens rotate on a cone to an opposite tilt (middle line). As mesogens and polysiloxane chains are nanophase separated this switching is not strongly affected by the polymer chains (see Figures 6,8);[98–100] (lower line) the transformation of the LC-polymers into an interlayer crosslinked elastomer (see Figure 8a) couples, however, the tilt direction of the different layers. Thus a higher force is necessary for switching from the orientation, in which the network is formed to the opposite orientation.[107,108]

tilt direction of the mesogens parallel to the smectic layers (see **Figures** 7,8).[98–100] It is thus not hindered by the polymer chains and oligomers and polymers behave rather similar.[98–101] It gets thus possible to get ferroelectric oligomers, which switch at room temperature.[5] And because of this steric separation of the sublayer of the polymer chains and the switching within the ferroelectric smectic layers, even crosslinked "diluted" polysiloxanes can be switched in electric fields.[107,108] Details of the full characterization of the associated ferro-electric properties can be found in refs. [98–101,104,105,107,108]

This differentiates crosslinked "diluted" polysiloxanes strongly from all nematic LC-polymers and from LC-polymers based on polyacrylate or methacrylate chains. During switching of nematic phases, the direction of the director rotates to the perpendicular position.[91] It can thus not happen without interaction with the polymer chains. In LC-polymers based on polyacrylate or methacrylate chains there is no significant demixing of mesogens and polymers and the direct interaction of both parts is much stronger. As a result, crosslinked nematic LC-polymers cannot be switched in bulk and some tendency for switching can only be observed in highly swollen systems.[102,109]

The formation of a siloxane sublayer parallel to the smectic layers allows also two topologically different types of crosslinking, a crosslinking that connects different smectic layers and the mesogens within them (inter-layer crosslinking) and a crosslinking preferably within the siloxane sublayer (intra-layer crosslinking) (see Figure 8). Both systems behave very differently regarding the influence of crosslinking on the ferroelectric switching of the chiral smectic C* phase. In intra-layer crosslinked systems, the switching time is nearly not effected by the crosslinking process, although it transfers a soluble polymer into a soft solid material.[110] In inter-layer crosslinked elastomers the switching time gets reduced and the network stabilizes the memory of the director orientation (and the tilt direction) present during network formation.[107,108,111] The crosslinking density determines thereby the strength of this stabilization (see Figure 7).[112] In addition typical dynamic modes of the ferroelectric phase like the "soft-mode" slows down during crosslinking.[113]

The separation of the smectic layers by a 2D sublayer of polysiloxanes leads—in addition—to a weaker coupling between the individual layers and this disturbs the transfer of the tilt direction between the layers. So there is evidence that—at least several—of the "diluted" ferroelectric polysiloxanes display chiral smectic phases of the "deVries" type.[104,105] And this is a signature of a weak coupling of the smectic layers across the siloxane sublayer. This becomes evident from a comparison of the ferroelectric properties around the phase transition from the smectic C* to the high temperature smectic A phase. Usually, this phase transition is second order. With increasing temperature, the tilt in the smectic C* phase decreases till the mesogens are finally standing upright and the ferroelectricity is gone. Thus, the macroscopic polarization and the hysteresis decrease continuously to zero. In systems with a "deVries" type phase transition the phase transitions happen however, just by a loss of the correlations of the tilt direction between the different layers. Thus, the tilt per layer stays constant, but the macroscopic tilt disappears, because each smectic layer gets a different tilt direction and thus a different direction of the electric polarization. Careful characterization of chiral smectic phases from various "diluted" polysiloxanes show that their phase transition is of the "deVries" type.[104,105] Such phase transitions are interesting as they are accompanied only a very small change of the smectic layer thickness at the transition from smectic A to the chiral smectic C* phase.[106] This is advantageous for display

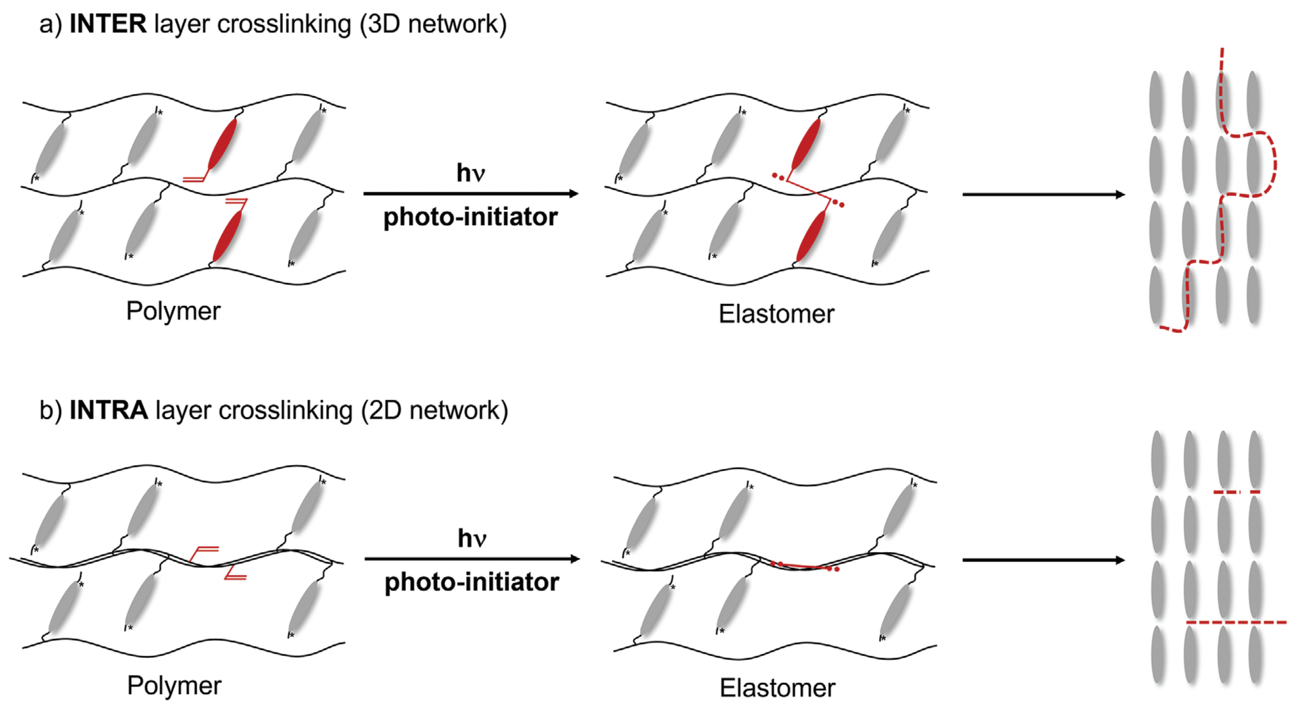

Figure 8. a) LC-polysiloxanes with the crosslinkable unit (acrylate or acrylamide) at the end of the mesogens form a 3D network by inter layer crosslinking[108,114] (compare Figure 2b, right). In it different layers get covalently coupled; b) on the contrary, LC-polysiloxanes with the crosslinkable units close to the siloxane chains form predominantly a 2D network structure, in which there is very little coupling between the different layers.[110]

applications. In addition the associated smectic A phases show very strong electro-clinic effects.[104,105]

Due to their high mobility and the high stability of the smectic phases "diluted" LC-polysiloxanes can be processed into "free standing" smectic films.[114–116] These are highly oriented (smectic layers parallel to the surface) only nanometer thick films, whose thickness is a multiple of the thickness of the individual smectic layer.[106] They can be prepared—in analogy to the technic developed for low molar mass smectics—by "drawing the melted bulk material" over a hole (eventually followed by blowing).[114,115,117,118] Alternatively they can be prepared by spin coating on a substrate, which can be removed afterward.[116] This last method, which uses the polymer properties to stabilize the thin film, can also be applied to LC-ionomers (discussed above).[78,79]

Besides allowing a basic characterization of the smectic phases, free standing films and free standing bubbles are an excellent tool to characterize the mechanical properties (elasticity) of crosslinked smectic elastomers.[114] In this way it was possible to demonstrate that LC-elastomers from homo-polymers and "diluted" copolymers behave rather differently.[105] In addition they allow the preparation of free films, which can be removed, translated, or further processed afterward.[115,116]

So as a result, the nanophase separated smectic structure in "diluted" LC-polysiloxanes makes it possible to decouple mobility and switching in the sublayers of the chiral mesogens and mechanical stability in the crosslinked sublayers of the polysiloxanes. In addition, the presence of "deVries" type smectics creates materials with a very big electro-clinic effect.

6. Smectic Block-Copolymers with LC and Non-LC Components

A different situation for smectic phases in combination with nanophase separation is realized in block-copolymers. Here either one block or both blocks can be LC (preferably a smectic LC-polymer). In addition a combination with an amorphous polymer is possible. If a well-defined superstructure between both blocks is desired, such polymers have to be made by well-established living polymerization technics. Anionic polymerization is, however, hardly compatible with the functional groups present in mesogens. So these polymers were made—at the beginning—in a two stage process, first preparing a block-copolymer and then linking functional mesogenic units to one of the blocks.[119–124] In recent years the synthesis of such block copolymers was changed to methods of controlled radical polymerization or ring-opening-metathesis-polymerization.[125–129] This made a direct synthesis of many block-copolymers possible and led to the first systems, in which both blocks are LC.[125,127–129] This can be i) polymers with two rod-like LC-blocks, ii) polymers with two or three blocks of LC-side chain polymers, or iii) polymers, which combine a central block of the LC-main chain type and two peripheral blocks of the LC-side chain type.[125,127,128,130,131]

The interest in these systems is a study of the interplay of the two-phase morphology (size range many nm, ideally lamellar), due to demixing of the incompatible blocks and the LC phases present in at least one block (smectic layer structure less than a nm). The questions to be answered are: does the existence of a LC phase change the type of two-phase morphology and is

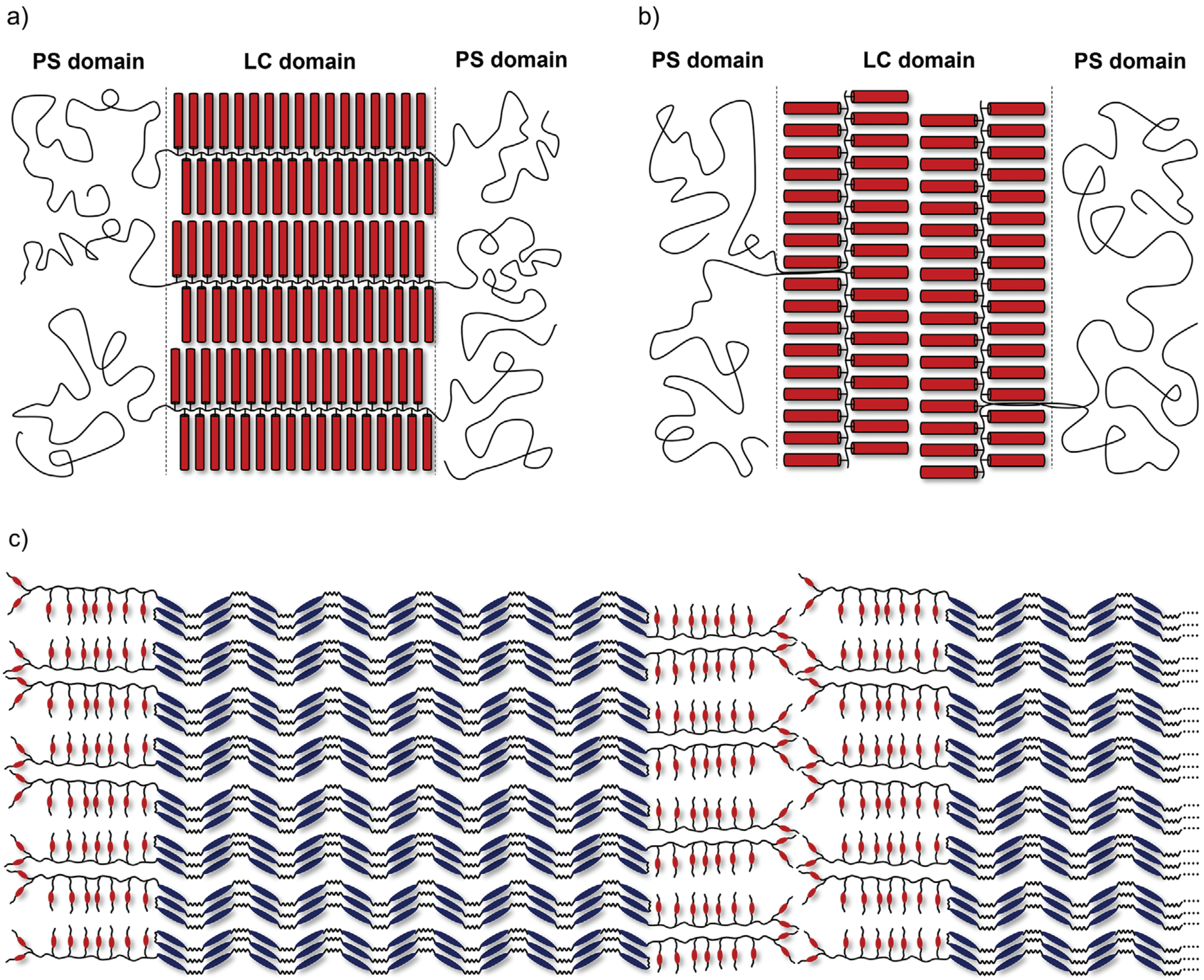

Figure 9. Different possibilities for the orientation of smectic layers and the two-phase morphology with respect to each other in LC block-copolymers. a) Most often observed morphology in lamellar block-copolymers prepared from polystyrene (amorphous) and a smectic LC-block; this orientation happens because the smectic layers tend to orient perpendicular to the lamellar phase morphology.[121] b) Sometimes observed orientation.[121] c) Situation in block-copolymers consisting from an LC-main chain block and an LC-side chain block.[125,127]

there an orientational correlation between the smectic layering and the two-phase morphology (e.g., lamellar). Many basic structure-property relations could already been studied with the first block-copolymers, which combined smectic side chain and amorphous polymer blocks (see **Figure 9**).[120–122] Thereby it turned out that the presence of a LC phase shifts—of course—the expected phase morphology to some extent.[121,125] In addition the layers of the block-copolymer and the smectic layers can orient parallel or perpendicular to each other, depending on the connectivity of both blocks and the morphology of the two phase structure. On the molecular level the polymer chains like to cross the interface in a straight way (Figure 9). As the mesogens will orient preferably perpendicular to the polymer chain, this leads to a tendency for perpendicular orientation between the interface between both blocks and the smectic layers. For a lamellar block morphology this orientation with both layers oriented perpendicular to each other has been observed.[121] For a block-copolymer morphology with long polystyrene rods in the smectic matrix however a different orientation was observed. Here the smectic layers orient parallel to the interface between both blocks.[121]

Such block-copolymers have been studied for different applications. One is the attempt to prepare macroscopically hard materials (high T_g amorphous phase), which can still be switched in electric fields.[123,124] For these systems it can be shown that the resulting phase separated nanostructure can be reoriented/switched in electric fields, if the LC-block forms a low T_g ferroelectric chiral smectic C* phase. Such types of block-copolymers can also be used to induce a "random planar orientation" of the smectic structure parallel to the substrate.[132] Such a structure is, for example, attractive for a photoalignment of the LC-director. It is induced by the tendency of the amorphous polymer to wet substrate and air interface.[132] This type of orientation is thereby based on the same arguments as the homeotropic alignment of "diluted polysiloxanes" discussed before.[116] Also in their case, the siloxane sublayer wets substrate and air, but it orients—in this case of a statistical copolymer—parallel to the smectic layers (see Figure 6). LC block-copolymers have also been used to prepare thin films with channels filled with polymeric ionic liquids (NO LC).[126] It is thereby the advantage that the block-copolymer can change its two-phase morphology on clearing of the LC phase.[126] This produces a switch to change the ionic conductivity of the film as a function of temperature.

Regarding the mutual interaction of the orientation within both blocks, block-copolymers consisting of a central LC-main chain like segment and to peripheral LC-side chain blocks are most interesting (see Figure 9c).[125,127] In this case the competition between a continuous LC-director or the transition of the main chain between both phases (it will orient perpendicular to the smectic layers in the LC-main chain block and parallel in the LC-side chain block) is dominant. Experiments show that in this system the continuous transition of the main chain at the interface dominates for most block compositions.[125] Thus the smectic layers in both blocks orient perpendicular to each other (Figure 9c).

This packing requires also that there are many hairpin conformations in the spacer of the LC-main chain polymer. This corresponds to the situation depicted in Figure 4, where such a conformation is discussed for LC-main chain polymers with various types of defects in the spacer (no straight *n*-alkan).

For diblock-copolymers with two smectic blocks consisting of the same type of LC-polymer the situation is different.[130,131] Here the director usually just extends from one subphase to the other. Such systems, in which only one LC-block contained azo-type mesogens (and the other classical mesogens), have been studied regarding photoalignment. And it could be shown that the LC-director oriented homogenously throughout the sample. If the azo-mesogen is linked to the main chain only by H-binding, it can be removed by washing after photoalignment.[130] Such block-copolymers could then be used to prepare well oriented, highly birefringent polymer films, which are colorless (and thus no longer sensitive to UV-irradiation) after washing.[130]

7. Conclusion

LC-polymers show—on the one side—a large range of LC phases in full analogy to the phases found in low molar mass compounds. At the same time, however, also some polymer-specialties are observed, which are discussed here for smectic (layered) LC-phases. Generally, such specialties are more easily observed for smectics, compared to nematics, as the order in smectics is higher and thus differences are more easily recognized.

The differences discussed here are mostly related either to the i) effect of crosslinking (a specialty of polymers) and/or the ii) presence of subunits with rather different solubility/polarity, which leads to the formation of different sublayers within the smectic phase. Concerning the effect of crosslinking (i), this depends strongly on the crosslinking density. In slightly crosslinked LC-networks (that is in crosslinked elastomers, in which the length of the linear chains between the netpoints—equal to distance between the netpoints—is rather long) the network can stabilize the smectic structure. This happens because crosslinking leads to a long-range correlation between the individual smectic layers. This can increase the smectic long-rang order. On the other side, a denser crosslinking limits the "perfectness" of the smectic order, because all netpoints act also as localized defects. Independent of the perfectness of the smectic layer structure, densely crosslinked smectic materials are fascinating materials for the separation of small molecules.

The presence of subunits with rather different solubility/polarity (ii), will—on the other side—lead to the formation of different sublayers within the smectic phase, which may be composed of mesogens and bulky ionic groups or mesogens and incompatible polymer chains. It can lead to a modulation of the nanophase segregation within the smectic layers and includes often the formation of sublayers consisting of the poorly compatible non mesogenic parts of the polymer. It can be observed for semiflexible LC-main chain polymers and LC-side chain polymers. This allows a mixing of the LC-polymers with other polymers, which have a good affinity to the second sublayer. It also allows it to separate, to some extent, a network structure from the packing of the mesogens. As a result, "diluted" LC-polysiloxanes with a ferroelectric smectic C* phase can be transformed into elastomers, in which ferroelectric switching in external E-fields competes with the rubber elasticity of the polymer network. Such networks show also a strong shape variation in external electric fields. In addition, very thin, but stable smectic films with a thickness of only several smectic layers can be prepared. This makes smectic polymers attractive as actuators in the field of nano-science, also in combination with phase separated smectic block-copolymers.

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Conflict of Interest

The author declares no conflict of interest.

Keywords

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Rudolf Zentel studied chemistry at the Johannes Gutenberg-University Mainz (Germany) and received his Ph.D. in 1983 with Profs. Ringsdorf and Strobl. After a postdoctoral stay in Freiburg (Germany) and research stays at the "IBM Almaden Research Center" in San Jose (USA, 1989–1990) and Düsseldorf (1990–1992) he got his first professorship in Mainz in 1992. After a stay in Wuppertal (1996–2000), he came back to Mainz in 2000. He was—from the beginning—involved in work on liquid crystalline polymers, their synthesis, physico-chemical properties, and structure–property relations.