Ionic Liquid Crystals

Koen Binnemans*

Katholieke Universiteit Leuven, Department of Chemistry, Celestijnenlaan 200F, B-3001 Leuven, Belgium

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1. Introduction

Liquid crystals are considered as the "fourth state of matter".¹ Their properties are intermediate between that of the crystalline solid state and that of the liquid state. Liquid crystals flow like a liquid, but they are anisotropic compounds.^{2,3} The refractive index, the electric permittivity, the magnetic suscep-

*Fax:+32 16 32 79 92. E-mail:Koen.Binnemans@chem.kuleuven.be.

Koen Binnemans was born in Geel, Belgium, in 1970. He obtained his M.Sc. degree (1992) and Ph.D. degree (1996) in chemistry at the Catholic University of Leuven, under the direction of Prof. C. Görller-Walrand. In the period 1999–2005, he was a postdoctoral fellow of the Fund for Scientific Research Elanders (Belgium) He did postdoctoral with

University of Leuven, under the direction of Prof. C. Görller-Walrand. In the period 1999–2005, he was a postdoctoral fellow of the Fund for Scientific Research Flanders (Belgium). He did postdoctoral work with Prof. Jacques Lucas (Rennes, F) and Prof. Duncan W. Bruce (Exeter, UK). In 2000, he received the first ERES Junior Award (ERES: European Rare-Earth and Actinide Society). From 2002 until 2005, he was (parttime) associate professor. Presently, he is Professor of Chemistry at the Catholic University of Leuven. His current research interests are metalcontaining liquid crystals (metallomesogens), lanthanide-mediated organic reactions, lanthanide spectroscopy, supramolecular coordination chemistry, photoluminescent materials, and ionic liquids. His other interests include reading, collecting minerals, and the history of artificial lighting.

tibility, and the mechanical properties of a liquid crystal depend on the direction in which these quantities are measured. Typical liquid crystals have either a rodlike or disclike shape, although many exceptions on this basic motif have been described.⁴⁻⁷ Most liquid crystals are neutral organic compounds. In metallomesogens, a metal is incorporated in the molecule of the liquid-crystalline compound.⁸⁻¹⁹ Also minerals or inorganic compounds can form liquidcrystalline phases.^{20–22} Driving forces for the formation of a liquid-crystalline phase (mesophase) are interactions between the anisometric molecules (dipole-dipole interactions, van der Waals interactions, $\pi - \pi$ stacking, ...). Ionic liquid crystals are a class of liquid-crystalline compounds that contain anions and cations. The ionic character means that some of the properties of the ionic liquid crystals differ significantly from that of conventional liquid crystals. Typical for ionic liquid crystals is the ion conductivity. The ionic interactions tend to stabilize lamellar mesophases, but ionic liquid crystals also display uncommon mesophases such as the nematic columnar phase.

ax, +52 10 52 19 52, E-mail, Roen, Dimemans@chem.kuleuven.be.

Ionic liquid crystals can be considered as materials that combine the properties of liquid crystals and ionic liquids. Worldwide intense research activity in the field of ionic liquids is presently going on.^{23–30} The main driving force to explore ionic liquids is the fact that these compounds have a very low vapor pressure, so that they are candidates to replace volatile organic solvents in organic reactions. Because the properties of ionic liquids (miscibility with water and other solvents, dissolving ability, polarity, viscosity, density, ...) can be tuned by an appropriate choice of the anion and the cation, ionic liquids are often considered as designer solvents. These ionic liquids can also be used to immobilize transition metal catalysts in the liquid phase of biphasic catalytic reactions. Other applications include their use as solvents for extraction processes and as an electrolyte for batteries, fuel cells, and dye-sensitized solar cells.

This review gives an overview of thermotropic ionic liquid crystals, and it is intended to build a bridge between the research in the field of liquid crystals and that of ionic liquids. Because a substantial part of the research in the field of ionic liquid crystals has been performed before the exponential growth of ionic liquid research, connections between ionic liquid crystals with low transition temperatures and room temperature ionic liquids have not often been made. Only recently the advantages of having a mesophase in ionic liquids have been recognized. The literature is covered up to August 2005. As mentioned, the literature overview is restricted to thermotropic ionic liquid crystals, i.e., compounds that form a mesophase upon heating the solid state or upon cooling the isotropic liquid. Lyotropic ionic liquid crystals (i.e., ionic compounds that form a mesophase upon addition of a solvent, such as an ionic surfactant) are excluded because several reviews describing these compounds already exist and because their behavior is very different from that of thermotropic ionic liquid crystals and ionic liquids.^{2,31–33} Previous reviews that partially cover the field of ionic liquid crystals include those of Skoulios and Guillon,³⁴ Paleos,³⁵ Neve,¹⁰ Tschierske,³⁶ Hardacre,³⁷ Donnio et al.,¹⁵ Kato and Yoshio,³⁸ and Lin and Vasam.³⁹ It should also be mentioned that liquid-crystalline charge-transfer systems,⁴⁰ and hydrogen-bonded liquid crystals⁴¹⁻⁴³ show similarities to ionic liquid crystals. In chargetransfer systems, a mesophase is induced by or stabilized by either $\pi - \pi$ charge-transfer interactions, or electron-donor acceptor interactions. In hydrogenbonded liquid crystals, thermotropic mesophases are displayed by associations of a hydrogen-bond donor and a hydrogen acceptor. The building blocks of hydrogen-bonded liquid crystals are often not mesomorphic themselves, but the resulting supramolecular aggregates are.

2. Types of Mesophases

Ionic liquid crystals display a rich variety of mesophases.^{44,45} An overview of the most important mesophases is given in this section. Different classification schemes are possible for liquid crystals, but it is useful to discriminate between mesophases formed by rodlike (or calamitic) molecules and those formed by disclike (or discotic) molecules.



Figure 1. Schematic representation of the nematic phase (N).



Figure 2. Schematic representation of the smectic A phase (Sm A).

The nematic phase (N) is the least ordered mesophase exhibited by rodlike molecules. This phase can be considered as a one-dimensionally ordered elastic fluid, with orientational order of the molecules, but without long-range positional ordering. In the nematic phase, the rodlike molecules tend to align themselves parallel to each other with their long molecular axis on average parallel to a preferential direction (Figure 1). This preferential direction is called the "director" of the phase (denoted by $\tilde{\mathbf{n}}$). The rodlike molecules are free to rotate around the long molecular axis but to some degree also rotation around their short molecular axis can occur. It is not uncommon to observe short range smectic order in the nematic phase. A nematic phase is only in a very few cases observed for ionic liquid crystals, although this phase is omnipresent in the case of neutral mesomorphic organic compounds.

In the smectic mesophases, the mesogenic molecules are situated in layers. The smectic A phase (SmA) is the least ordered smectic phase. The molecules in the smectic A phase are arranged in layers and have on average their long molecular axis perpendicular to the layer planes. Or, in other words, the long molecular axis is on average parallel to the normal to the layer planes (Figure 2). If a compound shows smectic polymorphism, i.e., if more than one smectic phase is observed when the compound is heated, the smectic A phase is observed at the high temperature end of the smectic range. The molecules are arranged randomly within each layer, and they have a considerable freedom for rotation around their long axis and even for translation in the smectic



Figure 3. Schematic representation of the smectic C phase (SmC).

layer. The smectic layers are not well defined. They are rather flexible and often show a curved arrangement. Although the molecules are on average perpendicular to the layer planes, local deviations from this perpendicular arrangement can occur. A modified form of a smectic A phase is the smectic A₂ phase (SmA_2) . This is a bilayer smectic A phase. In this phase, the molecules are in repeating bilayer units. The smectic A phase is optically uniaxial and often shows a homeotropic texture between crossed polarizers. In this case, the smectic planes are parallel to the microscope glass slide and the optic axis is perpendicular to it. The homeotropic texture is observed as a dark field between crossed polarizers. By pressing with a needle on the cover glass, this alignment can be destroyed, and optical birefringence will be noticed. As will be discussed further in this text, the smectic A phases of ionic liquid crystals have a strong tendency to align homeotropically. Therefore, it is often very difficult to obtain a nice optical texture for the smectic A phase of an ionic liquid crystal. The smectic A phase is the most common phase for ionic liquid crystals.

The smectic C phase (SmC) is very similar to the smectic A phase but with the difference that the molecules are now not perpendicular to the layer planes but tilted (Figure 3). The tilt angle is the angle between the long molecular axis and the normal to the layer planes. In contrast to the smectic A phase, the smectic C phase is a rare mesophase for ionic liquid crystals.

Ordered smectic phases exhibit long-range bond orientational order of the molecules but short-range positional order within the smectic layers. In the smectic B phase (SmB) there is a 6-fold bondorientational order, which means that the lattice orientation is retained in the layers, but the translational order is lost within a few intermolecular distances (Figure 4).

Some highly ordered smectic phases are no longer considered as true liquid-crystalline phases but as anisotropic soft crystals or anisotropic plastic crystals.⁴⁶ These phases should be called crystal phases, and they are denoted by a letter code that refers to their historical classification as a smectic phase but without their smectic code letter Sm. Examples are the crystal B phase (B), the crystal E phase (E), and the crystal G phase (G). These phases were previously known as smectic B, smectic E, and smectic G



Figure 4. Schematic representation of the smectic B phase (SmB). The phase is viewed from the side (left) and from above (right).

phase, respectively. The old smectic nomenclature is still often used to denote these crystal phases. The crystal B phase should not be confused with the smectic B phase (hexatic B phase). The latter phase is a genuine liquid crystal phase. The soft crystal phases have true long-range positional order in the three dimensions. The crystal G phase is a threedimensionally ordered version of the smectic F phase. In the crystal E phase, the molecules have a "herringbone" or "chevron" packing. The phase has an orthorhombic lattice. The rotation of the molecules around their long molecular axis is strongly hindered.

Cubic phases are mesophases of cubic symmetry.^{47,48} Because of their high symmetry, their physical properties are no longer anisotropic. No defect texture is observed by polarizing optical microscopy, and the viewing field between crossed polarizers remains black. The cubic mesophases are very viscous, and often their formation kinetics are very slow. Although cubic mesophases are very common for lyotropic liquid crystals, where a cubic phase is possible between any pair of phases, there are only relatively few examples of cubic mesophases in thermotropic liquid crystals. In thermotropic calamitic liquid crystals, the cubic phase is observed usually above a smectic C phase and below a smectic A or a nematic phase, although it can also be formed as the first phase below the isotropic liquid. Whereas a cubic mesophase can relatively easily be detected when it is present between two anisotropic mesophases, it is difficult to observe the formation of the cubic phase when it is formed by cooling an isotropic liquid. In this case, a deformation of air bubbles in the melt is observed, as well as a sharp increase in the viscosity of the liquid. Identification of the symmetry of a cubic mesophase is possible only by X-ray studies on aligned monodomain samples. Formerly, the cubic mesophase formed by biphenylcarboxylic acids with lateral nitro or cyano substituents was known as smectic D phase.^{49,50}

Discotic molecules can also form a nematic phase: the discotic nematic phase (N_D) (Figure 5). In contrast to the nematic phase of calamitic molecules, only a few examples of the discotic nematic phase are known. In this phase, the short axes of the molecules are on average parallel to a preferential direction. In the columnar nematic phase (N_{col}), short columns are ordered in a nematic way (Figure 6). This phase is also called nematic columnar phase. A more



Figure 5. Schematic representation of the discotic nematic phase $(N_{\rm D}).$



Figure 6. Schematic representation of the columnar nematic phase $(N_{\rm col}).$



Figure 7. Schematic representation of the hexagonal columnar phase (Col_h) .

common way of organization of discotic molecules is in columnar phases. In the columnar phases, the discs are stacked one of top of another to form columns. The columns themselves can be arranged in different two-dimensional lattices. In the hexagonal columnar phase (Col_h), the molecules are stacked into columns that are further arranged into a hexagonal lattice (Figure 7). Other types of columnar phases are the rectangular columnar phase (Col_r) and the oblique columnar phase (Col_o). In some types of columnar phases, the order of the molecules within the columns is a-periodical (disordered columnar phase), while in other cases there is an ordered, regular stacking inside the columns (ordered columnar phase). In the older literature, the columnar phases are often denoted as "D" (from discotic) instead of "Col". This is confusing because a mesophase should be classified on the basis of its symmetry not on the basis of the shape of the constituting molecules. It can be difficult to recognize the symmetry of a columnar mesophase by polarizing optical microscopy. High-temperature X-ray diffraction is then necessary for mesophase identification.

3. Mesogenic Salts with Organic Cations

3.1. Ammonium Salts

Ammonium salts are well-known cationic surfactants. These amphiphilic molecules aggregate in aqueous solution to micelles and at higher concentrations to lyotropic mesophases.³¹ A typical member of this class of compounds is cetyltrimethylammonium bromide (CTAB) (1). Some surfactants, but not all, can also form thermotropic mesophases.



The *n*-alkylammonium chlorides, $C_nH_{2n+1}NH_3^+Cl^-$, are the simplest type of liquid-crystalline ammonium salt.^{51–54} These compounds can be prepared in anhydrous form by bubbling dry hydrogen chloride gas through a solution of *n*-alkylamines in dry trichloromethane, followed by recrystallization from trichloromethane and by drying in vacuo.⁵² Compounds with an alkyl chain between C₆H₁₃ and C₁₈H₃₇ have been investigated.⁵² The short chain compounds are slightly hygroscopic, but the long chain compounds are not. The compounds show a stepwise melting behavior; the solid compound is first transformed upon heating into a plastic phase with conformational disorder of the alkyl chains, followed by transformation to a smectic phase. The smectic phase is supposed to be structurally similar to the neat phase of anhydrous soaps (smectic A phase). Further heating causes formation of a clear, optically isotropic liquid, in which still some domains with smectic order of the molecules can be detected by X-ray diffraction.⁵² It was observed that cooling of the mesophase results in the formation of a solid with partially disordered alkyl chains.⁵³

Matsunaga and co-workers investigated the mesomorphism of the salts formed by the reaction between *n*-alkylamines and aromatic acids.^{55,56} All the liquidcrystalline salts exhibit a smectic A phase. Picric acid forms mesogenic salts with the long-chain amines n-heptadecylamine and n-octadecylamine (2), whereas benzenesulfonic acid already forms a mesophase with *n*-decylamine (3).⁵⁵ The smectic A phase formed by the salts of pyridine-3-sulfonate (4) is more stable than that of the corresponding salts of benzenesulfonic acid. This is attributed to hydrogen bonding between the ammonium ion and the pyridine nitrogen atom. This work was extended to the salts of naphthalene-1-sulfonic acid (5), naphthalene-2-sulfonic acid (6), and 1-naphthol-4-sulfonic acid (7).⁵⁶ Both the melting and clearing points are markedly higher for the naphthalene-2-sulfonates than for the naphthalene-1-sulfonates. It was assumed that the alkyl chains are interdigitated in the smectic A phase. The introduction of a hydroxyl group on the naphthalene ring has a strong influence on the mesophase behavior; for the 1-naphthol-4-sulfonate salts no mesomorphism was observed when the alkyl chain contained less than 13 carbon atoms. Starting from the $C_{15}H_{31}$ chain enantiotropic mesomorphism exists, and the temperature range over which the smectic phase is stable widens markedly with increasing chain length. Salts formed by the interaction of acid derivatives of guanine (8) and cytosine (9) with n-hexadecylamine exhibit smectic mesomorphism.⁵⁷ Also the equimolar mixtures of the guanine and cytosine salts are liquid-crystalline. By molecular recognition and hydrogen bonding, the salts for guanine-guanine (10) and cytosine-cytosine (11) homodimers, or guanine-cytosine (12) heterodimers.



Mesomorphism is also observed for certain *n*-alkylammonium tetrachlorometalate(II) complexes. The general formula of these compounds is $(C_nH_{2n+1}NH_3)_2[MCl_4]$, where M = Zn, Cd, Hg, Cu, Pd, Co, Fe, Ni, Mn, Pb.^{58–73} These compounds have a perovskite-type layer structure, which consists of inorganic ionic sheets of corner-sharing MCl₆ octahedra with a divalent metal in the center.^{58,63,66} The

cavities between the octahedral sites are occupied by the NH₃⁺ polar headgroups of the *n*-alkylammonium moieties. The hydrogen atoms of the ammonium groups are hydrogen bonded to the chloride ions of the MCl₆ octahedra. The inorganic layers are sandwiched between a bilayer of alkyl chains. The distance between the layers depends on the length of the alkyl chain. In $(C_{12}H_{25}NH_3)_2[ZnCl_4]$, discrete [ZnCl₄]²⁻ tetrahedra are present, instead of interconnected octahedra.⁶³ There has been a strong interest in these compounds due to their solid-state polymorphism, which corresponds to a gradual increasing disorder of the alkyl chains upon heating (orderdisorder phase transitions). The $(C_nH_{2n+1}NH_3)_2[MCl_4]$ compounds are considered as simple solid-state models of a lipid bilayer. It was argued that by studying the phase transitions in these compounds, a better understanding of the phase transitions in lipid bilayers could be achieved. In the high-temperature polymorphs, the alkyl chains show increasing conformational disorder, while the ionic regions of the structures remain virtually unchanged. When the alkyl chains are in a liquidlike molten state and when the inorganic ionic layer is still intact, the resulting phase can be considered as a smectic phase. However, in contrast to the large number of studies on the solid-state polymorphism of the $(C_nH_{2n+1}NH_3)_2[MCl_4]$ compounds, data on the mesomorphism of these compounds are scarce.^{62,66} This is mainly due to relatively low thermal stability of these complexes. It is striking that polarizing optical microscopy studies have been neglected during the investigations of these compounds, although this technique is very valuable for the detection of mesophases. It is evident that further work is needed to elucidate the mesophase behavior of the $(C_nH_{2n+1}NH_3)_2[MCl_4]$ complexes. Needham et al. mention that some inconsistencies in the data obtained by different authors can be traced back to impure samples.⁷¹ Landi and Vacatello observed liquid-crystalline behavior for the $(C_{16}H_{33}NH_3)_2[MCl_4]$ compounds, when M = Co, Zn, Fe, and Hg, but not when M = Cu, $Mn.^{62}$ Although most of the work on the tetrahalometalates concerns the tetrachlorometalates, it is also possible to prepare the corresponding tetrabromometalates. Busico et al. described a smectic mesophase for the series $(C_nH_{2n+1}NH_3)_2[ZnBr_4]$.⁷⁴ The presence of the hydrogen bonding in the $(C_nH_{2n+1}NH_3)_2[MCl_4]$ compounds promotes crystallization and often prevents the formation of a mesophase or an isotropic phase with high fluidity.

The *n*-alkylammonium pyroglutamates (13) exhibit a smectic A phase.^{75,76} The pyroglutamate anion is not only a bulky anion, but it can also dimerize through intermolecular hydrogen bonding. Both racemic and enantiopure compounds have been investigated.

The mesophase behavior of the quaternary ammonium salts has been investigated in much more detail than that of the salts of primary amines. Iwamoto and co-workers have studied the thermal behavior of the *n*-alkyltrimethylammonium chlorides, bromides, and iodides.⁷⁷ They attribute a solid-solidphase transition to melting of the alkyl chains, but they do not consider the phase that is formed as a liquid-crystalline phase. The detailed study of the high-temperature phases was hampered by thermal decomposition of the compounds. Paleos and coworkers mention that the *n*-alkyltrimethylammonium bromides are thermally unstable and decompose before melting.⁷⁸ However, replacement of one of the methyl groups by a longer chain improved the thermal stability. A smectic mesophase was detected for dimethyl dodecyl *n*-propylammonium bromide (14) and dimethyl dodecyl 3-hydroxypropylammonium bromide (15). Because of hydrogen bonding, dimethyl dodecyl 3-hydroxypropylammonium bromide has a wider mesophase stability range and a higher clearing point than dimethyl dodecyl-*n*-propylammonium bromide. This work was extended to other functionalized quaternary dimethylammonium salts with polar groups (hydroxyl, carboxylic acid, or cyano groups),^{79–85} or with a terminal double bond (16, 17).^{85–87} The thermotropic behavior of alkylammonium alkanesulfonates⁸⁸ and alkylammonium benzenesulfonates⁸⁹ was investigated by Matsunaga and co-workers. Triethyloctylammonium hydroquinonesulfate is liquid-crystalline at room temperature, and it exhibits a smectic mesophase.⁹⁰ Trimethylhexadecylammonium hydroquinonesulfate forms a mesophase above 80 °C, whereas tributyloctylammonium hydroquinonesulfate and tributyldodecylammonium hydroguinonesulfate are not mesomorphic.91



A new type of ordered smectic mesophase, the smectic T phase, was discovered in the N,N-dialkyl-N,N-dimethylammonium bromides.⁹² An example is N,N-ditetradecyl-N,N-dimethylammonium bromide (18). It is not necessary that the two long alkyl chains contain the same number of carbon atoms. The X-ray patterns of the smectic T phase show typically sharp Bragg reflections in the small-angle region with reciprocal spacings in the ratio 1:2:3:4:5 (indicative

for a lamellar phase) and also rather sharp Bragg reflections in the wide-angle region with reciprocal spacings in the ratio $\sqrt{2}:\sqrt{4}:\sqrt{5}$ (indicative for a tetragonal lattice). This phase involves single layers of tetragonally arranged ammonium and bromide ions separated by sublayers of disordered alkyl chains. When a cyano group is present at the terminal position of one of the alkyl chains, a smectic A phase rather than a smectic T phase is observed.^{83,84} Skoulios and co-workers also found the smectic T phase below a smectic A phase in long alkyl-chain quaternary ammonium salts bearing two hydroxyethyl groups at the polar headgroup.⁹³ Another class of compounds that exhibits a smectic T phase are the 1,4-dialkyl-1,4-diazoniabicyclo[2.2.2]octane dibromides (19; R = $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$).⁹⁴ This phase was overlooked in the original account on the mesophase behavior of these compounds,⁹⁵ which show a strong tendency to spontaneous homeotropic alignment. The 1,4-dialkyl-1,4diazoniabicyclo[2.2.2]octane dibromides show this homeotropic alignment, even when they are entering into the smectic T phase from the crystalline phase. A smectic T phase is also exhibited for a series of 1.4piperazinium di-*n*-alkyl sulfates (**20**; $R = C_{10}H_{21}$, C₁₂H₂₅, C₁₄H₂₉, C₁₆H₃₃).⁹⁶ An ordered tetragonal smectic phase, similar to the smectic T phase was observed for dialkyldimethylammonium bromides bearing a 4,4'-oxynitrostilbene mesogenic group (21).⁹⁷



For the di-*n*-alkyl dimethylammonium bromides, where the alkyl chain is a tetradecyl or octadecyl chain, a smectic A_2 phase is found, but this phase shows less interdigitation than the ammonium salts with one alkyl chain.⁹⁸⁻¹⁰⁰ Benzyltrioctadecylammonium bromide (**22**) forms a smectic A_2 phase (SmA₂).^{101,102} Although trimethyl *n*-octadecylammonium chloride, (C₁₈H₃₇)(CH₃)₃N⁺Cl⁻, shows no liquid– crystalline phase, the corresponding tetrachlorometalate complexes, $[(C_{18}H_{37})(CH_3)_3N]_2[MCl_4]$ (23; M = Co, Ni, Cu, Zn, Cd), exhibit a smectic A phase.¹⁰³ This phase was also observed for the $[(C_{18}H_{37})_2]$ - $(CH_3)_2N]_2[MCl_4]$ complexes. The $[(C_{18}H_{37})(CH_3)_3N]_2$ -[MCl₄] have a stronger tendency to form a mesophase than the above-mentioned $(C_nH_{2n+1}NH_3)_2[MCl_4]$ complexes because replacement of the protons by methyl groups inhibits the formation of a hydrogen-bonded network between the cationic ammonium headgroups and the chlorine atoms of the tetrachlorometalate layer. A distinct SmA-to-SmA phase transition was observed for several tetrachlorometalate complexes. This phase transition is evident from a discontinuous change in the smectic layer thickness as a function of the temperature. The intensity of the X-ray diffraction peaks was much higher for the high-temperature smectic A phase than for the low-temperature smectic A phase. This lead to the conclusion that the smectic A phase at high temperature is more ordered than the smectic A phase at lower temperature. This behavior showing two different smectic A phases in one sample is uncommon. It is not clear yet how the two smectic A phases differ structurally. Not all tetrachlorometalate compounds show the smectic A polymorphism of the [(C₁₈H₃₇)₂(CH₃)₂N]₂-[CoCl₄] compounds; it is not observed for $[(C_{18}H_{37})_2$ - $(CH_3)_2N]_2[NiCl_4]$ series.



The symmetrical tetra-*n*-alkylammonium halides do not exhibit a liquid-crystalline phase, not even the compounds with long alkyl chains.¹⁰⁴⁻¹⁰⁷ Nevertheless, the tetra-*n*-alkylammonium halides exhibit a complex thermal behavior. The tetra-*n*-alkylammonium halides with short alkyl chains (methyl, ethyl, propyl) do not melt, nor do they show conformational disorder upon heating. They transform into plastic crystals at a single disordering transition, followed by sublimation or thermal decomposition. The tetra-*n*-alkylammonium halides with long alkyl chains (octyl chain or longer) show conformational disorder and motion before melting to an isotropic liquid. They do not exhibit a plastic crystalline state. The compounds with intermediate alkyl chain lengths (butyl, pentyl, hexyl, heptyl) exhibit both plastic crystalline phases and conformationally disordered phases.

It is possible to prepare quaternary ammonium salts bearing a cholestanyl group.¹⁰⁸ These compounds are gelators for a variety of organic solvents. Cholestanyl bis(octadecyl)ammonium iodide (**24**) shows a smectic phase, but the structurally related cholestanyl bis(octadecyl)methylammonium iodide (**25**) is not mesomorphic.^{108,109}



Vill and co-workers investigated the salts formed by the reaction of 1-amino-1-deoxy-glucitol (glycamine) and various organic acids.¹¹⁰ The alkanoate salts form a smectic A phase over a broad temperature range (26). Whereas the glycamine salt of 4-noctadecyloxybenzoic acid (in 1:1 ratio) forms a smectic A phase, a columnar phase was observed for mixtures where either an excess of the acid or an excess of glycamine was present. N-alkyl glucamines exhibit columnar phases with 4-n-alkoxybenzoic acids and with bis(dodecyl)phosphoric acid. Salts formed by the reaction between ethanolamine and an alkanoic acid are liquid-crystalline as well.¹¹⁰ The salts obtained by the reaction between cholesteryl hydrogen phthalate and *n*-alkylamines are liquid-crystalline, and the mesophase can easily be frozen into an anisotropic glass.¹¹¹ A smectic C phase was observed for α -[bis(2-hydroxyethyl)amino]- ω -(4'-methoxybiphenyl-4-oxy)alkane hydrochlorides (27).¹¹² The melting point of the salts decreases with increasing alkyl chain length. Ujiie and Yano detected a smectic A phase for a hydrophilic poly(ethylene imine) chain with hydroxy side groups attached to a nitroazobenzene mesogenic group (28).¹¹³ Smectic, cubic, and hexagonal columnar phases are exhibited by zwitterionic long chain alkyl dimethylammoniumalkoxydicyanoethenolates (29).¹¹⁴ These zwitterions have a very high dipole moment μ (> 25 D), and the



resulting strong dipolar interactions are the driving force for the liquid-crystalline behavior of these compounds.







Paleos and co-workers investigated the mesophase behavior of α - ω -diquaternary ammonium salts (30-**35**).¹¹⁵ By increasing the spacer length between the two quaternary nitrogen atoms, the melting and clearing point were lowered and more stable mesophases were obtained. Triethylammonium headgroups lead to more stable mesophases than did trimethylammonium headgroups. On the other hand, mesomorphism was absent in the compounds with a bulky diallylethylammonium headgroup (34-35). Thermotropic and lyotropic mesomorphism was observed for diaquaternary ammonium salts with mesogenic 4-cyanobiphenyl groups (36).¹¹⁶ The compounds exhibit an ordered smectic phase that has similarities with the smectic T phase described by Skoulios and co-workers.⁹² The ionic headgroups form an ordered tetragonal array, but the alkyl chains have some disorder. The lyotropic mesomorphism of triethylammoniodecyloxycyanobiphenyl bromide was investigated.¹¹⁷ The compound forms a lamellar phase in water. Addition of the thermotropic liquid crystals 5CB and 7OCB stabilized the lamellar lyomesophase, whereas addition of hexane had a destabilizing effect. Similar quaternary ammonium salts with a pendant cyanobiphenyl group have been used to obtain liquid crystal/clay mineral composites.^{118,119} Diquaternary ammonium surfactants in which the spacer consists of an oligo(oxyethylene) chain exhibit both thermotropic and lyotropic mesomorphism (37).¹²⁰ The complex 38 formed by the interaction between benzenehexacarboxylic acid (mellitic acid) and didodecyldimethylammonium bromide

exhibits a bilayer SmA₂ phase.¹²¹ Two types of lamellar thermotropic mesophases were detected. The complex *N*,*N*'-bis(2-(trimethylammonium)ethylene)-perylene-3,4,9,10-tetracarboxyldiimide-bis(2-ethylhexyl)sulfosuccinate) (**39**) shows an oblique columnar mesophase, with $\pi - \pi$ stacking of the perylene units.¹²² The same complex exhibits a lyotropic mesophase in DMSO. An ionic liquid crystal with a lamellar phase was obtained by interaction between a water-soluble tricycloquinazoline derivative and dialkyldimethylammonium bromide surfactants





(**40**).¹²³ The presence of a lamellar phase for these discotic mesogens was surprising, because one would expect to arrangement of the molecules into columnar phases.

Few data are available for liquid-crystalline salts of aniline derivatives. A smectic A phase was observed for 4-*n*-butoxyaniline hydrochloride (**41**) and 4-*n*-hexyloxyaniline hydrochloride (**42**).¹²⁴ Salts of alkyl esters of *p*-aminobenzoic acid with *p*-chlorobenzoic acid exhibit a smectic A phase (**43**).¹²⁵





3.2. Phosphonium Salts

The phosphonium salts are in many aspects comparable to the corresponding ammonium salts, although there are subtle differences. However, the mesophase behavior of the phosphonium salts has been studied in much less detail than the mesophase behavior of the ammonium salts. This is probably because the synthesis of phosphonium salts is more difficult than the synthesis of ammonium salts, due to the limited availability of the trialkylphosphines as starting materials. Kanazawa et al. have studied the thermal behavior of dimethyl di-*n*-alkylphosphonium chlorides, where the long alkyl chain is $C_{10}H_{21}$ (44), $C_{14}H_{29}$, and $C_{18}H_{37}$.¹²⁶ All the thermotropic phosphonium salts exhibited a smectic A phase. The mesophase range is wider than that of the corresponding ammonium salts, and the clearing point occurs at higher temperatures. Moreover, the phosphonium salts show a high thermal stability. A study of the nonlinear optical properties of dimethyl di-n-alkylphosphonium chlorides and dimethyl di-nalkylammonium chlorides in the vitrified mesophase state revealed that second harmonic generation (SGH) could be observed for the phosphonium salts but not for the ammonium salts.^{127,128} These results indicate that the phosphonium salts self-assemble in the mesophase to a noncentrosymmetric macroscopic arrangement of ions in an ionic (bilayer) structure. The spontaneous polarization occurs by the spontaneous displacement of the smectic layers. The differences between the behavior of the ammonium and phosphonium compounds were attributed to the fact that for phosphor the 3d orbitals can participate in the bonding, whereas this is not the case for nitrogen. DFT calculations in which the chlorine displacement in the linear $[PH_4-Cl-PH_4]^+$ was varied show that the stable geometry corresponds to a noncentrosymmetric atomic arrangement. This can give an explanation for the spontaneous displacement of the ions in the phosphonium salts.

Weiss and co-workers have investigated quaternary phosphonium salts with one, two, three, and four long alkyl chains.^{102,129,130} The phosphonium salts with one long alkyl chain form smectic A_2 phases with a strong interdigitation of the alkyl chains. The anhydrous forms of methyl tri-*n*-decylphosphonium chloride and bromide are not mesomorphic but form soft solid phases.¹²⁹ However, the monohydrates of these compounds are room temperature liquid crystals and form a smectic A_2 phase. This shows that



the water molecules are essential for the formation of a mesophase. Probably this is due to hydrogen bonding between the halide anions and the water molecules, which stabilizes the smectic layers. Methyl tri-*n*-decylphosphonium nitrate (45) is a solid at room temperature and forms a mesophase at about 60 °C. Small amounts of acetonitrile (ca. 1 wt %) lower the transition temperatures drastically, and the melting point becomes subambient. It is assumed that in the presence of acetonitrile liquid-crystalline clathrates are formed. The authors propose to use the methyl tri-*n*-alkylphosphonium salts as ordered solvents for UV-Vis studies and as a solvent for NMR spectroscopy. Benzyltrioctadecylphosphonium bromide is much more stable to heat than benzyltrioctadecylammonium bromide, but the temperature range of the mesophase is larger for the ammonium compound.^{101,102} Just as for benzyltrioctadecylammonium bromide, benzyltrioctadecylphosphonium bromide (46) exhibits a smectic A₂ phase. So far, no mesophases have been observed for the symmetrical tetra-nalkylphosphonium halides.¹⁰⁷ Amphiphilic phosphonium salts show antibacterial activity.¹³¹



3.3. Imidazolium Salts

Different types of substituted imidazoles can form ionic liquids and ionic liquid crystals by quaternization, but so far most studies on the thermal behavior of imidazolium salts have been restricted to 1-alkyl-3-methylimidazolium salts (47). The melting point shows the tendency to decrease with increasing alkyl chain lengths and reaches a minimum for alkyl chains of about eight carbon atoms.^{132,133} Further increase of the chain length leads again to an increase of the melting point. The van der Waals interaction also increases with increasing alkyl chain lengths, and for chain lengths of about 12 carbon atoms this van der Waals interaction between the alkyl chains promotes microphase separation of the hydrophobic alkyl chains and the charged parts of the molecules. This leads to the formation of lamellar mesophases. The 1-alkyl-3-methylimidazolium salts with alkyl chains ranging between C_4H_9 and $C_{10}H_{21}$ have a stronger tendency to supercool to a glassy state than the compounds with shorter and longer alkyl chains. In fact, it is often very difficult to force the imidazolium salts with medium-size alkyl chains to crystallize out. This is especially the case when the imidazolium salts are liquid at room temperature. Branching of the alkyl chain leads to higher melting points, due to a more efficient packing of the compounds with chain branching in the crystalline phase. For instance, for the different isomers of 1-butyl-3methylimidazolium hexafluorophosphate, the melting point of the compound with the n-butyl chain is 6.4 °C, whereas the melting points of the compounds with the sec-butyl and tert-butyl chains are, respectively, 83.3 and 159.7 °C.¹³⁴ It is also observed that the melting enthalpy increases with increasing chain branching. The melting point strongly depends on the choice of the anion. Imidazolium salts with fluorinated anions tend to have lower melting points than compounds with nonfluorinated anions. The symmetrically substituted 1,3-dialkylimidazolium salts have higher melting temperatures than the symmetrically substituted 1-alkyl-3-methylimidazolium salts. Replacement of the hydrogen atom at the carbon in the 2-position of the imidazolium ring by a methyl group or by a longer alkyl chain leads to higher melting points. Computational methods are available to predict the melting points of imidazolium salts or other ionic liquids with a rather good accuracy.^{135,136}

The first report on the existence of a mesophase in imidazolium ionic liquids with long alkyl chains was a communication by Bowlas et al.¹³⁷ These authors investigated 1-alkyl-3-methylimidazolium salts with chloride, tetrachlorocobaltate(II) (48) and tetrachloronickelate(II) (49) counterions. For ionic liquids having alkyl chains with less than 12 carbon atoms, no mesophase was observed. The compounds with $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, and $C_{18}H_{37}$ chain exhibit a smectic A phase with a large thermal stability range. The mesophase temperature range of the tetrachlorometalate(II) salts increases with increasing chain lengths. It was suggested to use these liquid-crystalline solvents for chemical reactions because the ordered nature of the solvent could have a catalytic role. Thermotropic mesomorphism was observed for the 1-alkyl-3-methylimidazolium tetrachloropalladate(II) salts, when the alkyl chain was either C14H29, C16H33, or C18H37 (50).138 The mesophase was identified as a fully interdigitated smectic A phase. For the compounds with $C_{10}H_{21}$ or $C_{12}H_{25}$ chains, solid-state polymorphism occurs, but a mesophase is absent. Gordon et al. investigated the mesophase behavior of 1-alkyl-3-methylimidazolium hexafluorophosphate salts $[C_n\text{-mim}][PF_6]$ (51).¹³² These compounds were prepared by a metathesis reaction between the corresponding imidazolium halide and HPF_6 . The compounds with alkyl chains shorter than $C_{14}H_{29}$ are not mesomorphic. The salts with an alkyl chain of 14 or more carbon atoms display an enantiotropic mesophase, which was identified as a smectic A phase. While the melting point increases only slightly with increasing alkyl chain length, the clearing point increases markedly. The compounds with the longest alkyl chains show thus a mesophase over a broader temperature range than do the compounds with shorter alkyl chains. No polymorphism was observed in the solid state. The mesophase of the $[PF_6]^-$ salts was found to be miscible with that of the corresponding [CoCl₄]²⁻ salts. The authors tried to reduce the melting point by making mixtures between 1-hexadecyl-3-methylimidazolium hexafluorophosphate and 1-hexadecylpyridinium hexafluorophosphate. No depression of the melting point was observed, but a slightly larger mesophase range was obtained for one of the mixtures. The crystal structure of $[C_{12}$ -mim] $[PF_6]$ shows the presence of discrete cation and anions, and consists of sheets of imidazolium rings and hexafluorophosphate ions, separated by interdigitated dodecyl rings.¹³² The imidazolium ring is planar, and the $[C_{12}$ -mim]⁺ cation is described as having a "spoon-shaped" structure. This shape is due to a disrupture of the straight nature of the dodecyl chain close to the ring, where it adopts a bent conformation. The dodecyl chains are tilted relative to the layers of the cations and anions. Holbrey and Seddon investigated the thermal behavior of 1-alkyl-3-methylimidazolium tetrafluoroborate salts, $[C_n-mim][BF_4]$ (n = 0-18) (52).¹³³ The imidazolium salts with the nitrogen atom substituted by a proton (n = 0) or by a methyl group (n = 1) are low melting crystalline solids. The salts with short alkyl chains (n = 2 - 11) are liquids at room temperature and form glasses on cooling to -80 °C, whereas the salts with longer alkyl chains (n = 12-18) are low melting solids that show a mesophase upon heating. On the basis of the defect texture observed by polarizing optical microscopy, the mesophase was identified as a smectic A phase. Whereas for the series with $[PF_6]^-$ counterions, a mesophase is only observed for alkyl chains with 14 or more carbon atoms, the corresponding $[BF_4]^-$ series already shows mesomorphism for a dodecyl chain (n = 12). Moreover, the tetrafluoroborate salts have lower melting points than the hexafluorophosphate salts. It is often difficult to observe good defect textures for the mesophase of these ionic liquid crystals by polarizing optical microscopy because of the tendency of the salts to form spontaneously a single homeotropic monodomain (which gives a dark field between crossed polarizers). Interestingly, Holbrey and Seddon noticed that better textures could be observed when the tetrafluoroborate salts were heated between two glass microscope slides, as opposed to the more typical microscope slide and cover slip.¹³³ The pressure of the heavier microscope slide on the sample breaks the homeotropic alignment.



De Roche et al. studied the phase behavior of 1-methyl-3-tetradecylimidazolium hexafluorophosphate and 1-hexadecyl-3-methylimidazolium hexafluorophosphate by different advanced analytical techniques including Raman spectroscopy, X-ray diffraction, and quasi-elastic neutron scattering (QENS).¹³⁹ They found a solid-phase transition that was not observed by Gordon et al.¹³² It was proposed that this transition involves structural rearrangements driven by a thermally activated increase of the molecular mobility. QENS data suggested that the increased motion of the alkyl chains is the main driving force for this solid-state transition. No major structural changes could be detected by single-crystal X-ray diffraction studies. The ionic conductivity in the high-temperature solid phase is so high that the authors considered these compounds as solid-state ionic conductors. This solid-state transition has been studied in detail at the molecular level by quantumchemical calculations.¹⁴⁰ These calculations show that the transition is associated with an interconversion between two stable conformations of the $[C_{14}\text{-mim}]^+[PF_6]^-$ ion pair. The mesophase of $[C_{16}\text{-}$ mim][PF₆] was identified as a smectic A phase.¹³⁹ Small-angle X-ray scattering studies¹⁴¹ and measurement of the ionic conductivity¹³⁷ indicate that some ionic aggregates must persist in the isotropic liquid phase of $[C_{16}\text{-mim}][PF_6]$.

To investigate the influence of the anion on the mesomorphic properties of the imidazolium salts, Bradley et al. prepared a series of 1-alkyl-3-methylimidazolium salts with varying alkyl chain length, and with chloride, bromide, triflate, and bis(trifluoromethanesulfonyl)imide anions.¹⁴² No mesophase could be observed for the compounds with bis(trifluoromethanesulfonyl)imide anions (53), whereas in the case of the triflate ([OTf]⁻) anions (54), only a small mesophase range was observed for the compounds with C₁₆H₃₃ and C₁₈H₃₇ chain, but no mesophase for compounds with shorter alkyl chains. The tetrafluoroborate, chloride, and bromide salts are mesomorphic for all the investigated compounds (with a dodecvl chain or a longer chain). Whereas the melting point increases slightly with increasing alkyl chain length, the clearing point increases more rapidly as a function of the chain length. The mesophase was identified as an interdigitated bilayer smectic A phase (SmA_2) . In the mesophase, the interlayer spacing increases monotonically with the alkyl chain length and decreases with increasing temperature, for each anion. The interlayer spacing also depends on the anion and increases in the order $[OTf]^- < [BF_4]^- < Br^- < Cl^-$. This order reflects the increase in ability of the anions to form a threedimensional hydrogen-bonding lattice. Just as in the case of $[C_{16}\text{-mim}][PF_6]$,¹³⁹ the layer spacing in the crystal is smaller than in the mesophase. The thermal behavior of the chloride and bromide imidazolium salts is more complicated than that of the fluorinated anions because chloride and bromide salts are very hygroscopic, and it is very difficult to obtain them in anhydrous form. The thermal properties of the anhydrous salts differ from those of the hydrated salts. For instance, the anhydrous salts have lower melting points and melting enthalpies than the corresponding hydrated salts. This can be attributed to the fact that the structure of the hydrated salts is stabilized by hydrogen bonding between the chloride (or bromide) ions and water molecules. The hydrated salts show a different thermal behavior after melting and cooling than before thermal treatment. Bradley et al.¹⁴² indicate that the chloride salts studied in the paper of Bowlas et al.¹³⁷ were in fact hydrated salts rather than anhydrous ones. A study of long-chain 1-alkyl-3-methylimidazolium chlorides indicates that the dependence of the thermal behavior of the hydrated chloride salts on the thermal history is due to conformational changes in the imidazolium groups.¹⁴³ Two different layered structures with a triclinic symmetry are observed for the chloride salts. The interlayer distance in one of the phases is about two times as large as in the other phase. This is explained on the basis of a structural model where one phase contains a bilayer structure with interdigitated alkyl chains and the other phase a bilayer structure with the alkyl chains packed end-to-end. Hydrogen bonding due to the presence of water molecules seems to play an important factor in the polymorphism of the imidazolium chloride salts. To understand the differences in the layer spacings, Li et al. used time-resolved X-ray scattering experiments to study the crystallization behavior of 1-hexadecyl-3-methylimidazolium chloride and 1-methyl-3octadecylimidazolium chloride.144 The SAXS and WAXS patterns were measured during isothermal crystallization experiments. Four phases with different thermodynamic stabilities were found: a triclinic extended bilayer structure, a triclinic double bilayer structure, an orthorhombic perpendicular double



Figure 8. Schematic representation of the relative stability and mutual transitions of the smectic phase and the four crystal phases in $[C_{16}$ -mim]Cl en $[C_{18}$ -mim]Cl. Reprinted with permission from ref 144. Copyright 2005 American Chemical Society.

bilayer structure, and a transient rotator double bilayer structure (Figure 8). The transient phase that appears at slight undercooling of the smectic phase seems to be thermodynamically unstable at any temperature. The molecules have a high mobility in the transient phase, and the structure of this phase is comparable with the rotator phases of *n*-alkanes. The transient phase serves as a nucleus for the formation of the three other crystal structures. Water present in the samples was found to have an effect on the size of the crystals that are formed in the transient phase. The influence of water on the structure is a kinetic effect. Small crystals are transformed into the triclinic extended bilayer structure, whereas large crystals are transformed into the orthorhombic bilayer structure. An X-ray reflectivity study on spin-coated thin films of 1-alkyl-3-methylimidazolium salts indicate that ordered films could only be obtained after the compounds were melted into the isotropic state and cooled to the mesophase or to a crystalline state.¹⁴⁵ This work also shows that the alkyl chains remain disordered when the imidazolium molecules crystallize from the mesophase. The salt-air and salt-substrate interfaces contain ionic groups. The interface contains thus cationic and anionic groups. The alkyl chains are oriented toward the bulk.



Although the relative position of the anions with respect to the imidazolium cations can be derived from the single-crystal structures determined from

imidazolium salts, one can expect that a large difference in positions exists in the solid and in the liquid state. However, neutron diffraction measurements on molten non-mesogenic 1,3-dimethylimidazolium chloride indicate that significant charge ordering is present in the liquid state and that the local order in the liquid state is similar to that observed in the solid state.¹⁴⁶ This is also in agreement with the findings of Bradley et al. that in the isotropic phase of long chain 1-alkyl-3-imidazolium salts some short-range associative structural ordering is still present.¹⁴²

The binary phase diagram of the mesomorphic ionic liquid 1-methyl-3-octadecylimidazolium tetrafluoroborate and the nonmesomorphic ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate shows that the smectic mesophase of [C₁₈-mim][BF₄] exists in mixtures that contain [C₂-mim][BF₄] up to a mole fraction of 0.6.147 However, the clearing point decreases rapidly with increasing amounts of $[C_2 \min[BF_4]$. The corresponding hexafluorophosphate salts show a mesophase in binary mixtures up to a mole fraction of 0.4 for $[C_2-mim][PF_6]$. The ionic conductivity of 1-methyl-3-octadecylimidazolium tetrafluoroborate and of its mixture with $[C_2-mim][BF_4]$ (3:2 molar ratio) has been measured. The ionic conductivity of homeotropically aligned samples in the smectic A phase was higher than that of polydomain samples. The presence of the more mobile ionic liquid [C2-mim][BF4] in [C18-mim][BF4] increases the ionic conductivity with 1 order of magnitude. Ohno and co-workers investigated the mesophase behavior of 1-ethyl-3-dodecylimidazolium dodecylsulfonate and its mixture with lithium tetrafluoroborate.¹⁴⁸ Addition of LiBF₄ increased the clearing point of the smectic A phase. This was attributed to a stronger intermolecular electrostatic interaction in the ionic layer due to the Li⁺ ion. At the same time, the mesophase showed more resistance to crystallization upon cooling. Anisotropic ion conduction was observed in the mesophase, and the conductivity was higher in the mesophase than in the isotropic state. 1-Alkyl-3-methylimidazolium salts with long alkyl chains and with tetrafluoroborate and hexafluorophosphate counterions have been used as a supporting electrolyte in polymer light-emitting diodes (PLEDs).¹⁴⁹ Only when the alkyl chain is a dodecyl or a longer chain, the ionic liquid is compatible with the light-emitting polymer. Ionic liquids with a short chain (butyl) give phase separation.

It is not necessary to have long alkyl chains on the imidazolium ring to induce mesomophism, provided that an anion with a long alkyl chain is used. For instance, 1,3-dimethylimidazolium dodecylsulfonate (**55**) exhibits a smectic A phase.¹⁵⁰ The phase behavior of the imidazolium dodecylsulfonate liquid crystals can be tuned by introduction of methyl groups on the imidazolium ring. Whereas a methyl group on the 2-position eliminated the liquid–crystallinity (**56**), a methyl group on the 4-position was effective to suppress the crystallization (**57**).

High-pressure carbon dioxide was found to reduce the melting point of the ionic liquid crystal [C_{16} mim][PF₆].¹⁵¹ At 70 bar of CO₂, the melting point of



this compound was reduced from 75 to 50 °C. The authors assume that CO_2 disrupts cation—anion and tail—tail interactions rather than simply playing the role of an impurity. The smectic A phase was still formed under these conditions.

Bünzli and co-workers investigated the spectroscopic properties of different europium(III) salts dissolved in 1-alkyl-3-methylimidazolium chloride and nitrate ionic liquid crystals.¹⁵² The neat ionic liquid crystals showed blue fluorescence (ligand emission) upon irradiation by ultraviolet light. Addition of an europium(III) salt partially quenched this blue fluorescence, but at the same time red europium(III)-centered luminescence was observed. This is due to energy transfer of the excitation energy from the organic chromophores to the europium(III) ion. By a proper choice of the excitation wavelength and counterion, the emission color could be tuned from blue to red. The main part of the work was focused on the chloride salts because these are room temperature ionic liquid crystals, whereas the corresponding nitrate salts are solid at room temperature. The dissolution of the europium(III) salts had only a minor influence on the mesogenic properties of the ionic liquid host, provided that the salt concentration was lower than 10 mol %. This indicates that the 1-alkyl-3-methylimidazolium chloride compounds have the possibility to solubilize substantial amounts of inorganic salts.

1-Citronellyl-3-tetradecylimidazolium bromide (58) is an example of a chiral compound that can be prepared from an easily accessible precursors from the natural chiral pool.¹⁵³ However, its smectic mesophase is not chiral. Neither was this compound as a chiral dopant able to induce a chiral phase in the smectogenic compound 1-dodecyl-3-methyl imidazolium bromide. The chiral 1-citronellyl-3-alkylimidazolium bromide salts with more than 14 carbon atoms in the alkyl chain do not exhibit a mesophase. The symmetric 1,3-di-citronnellyl-1H-imidazolium bromide (59) was not mesomorphic either. The 1-acetamido-3-alkylimidazolium bromide (60), hexafluorophosphate and tetrafluoroborate salts self-assemble thanks to the primary amide group to a hydrogenbonded ribbon polymer that shows a mesophase over a wide temperature range.¹⁵⁴ The mesophase is a smectic A phase in all compounds investigated. For the same alkyl chain length, the melting points increase in the order $[BF_4]^- < [PF_6]^- < Br^-$.



The majority of the smectic liquid-crystalline imidazolium salts described so far belong to the 1-alkyl-3-methylimidazolium type, but the thermal behavior of other types of imidazolium salts has been investigated as well. Dzyuba and Bartsch prepared 1,3-dialkylimidazolium salts with bromide and hexafluorophosphate counterions, and with alkyl chains up to C₁₀H₂₁,¹⁵⁵ but none of the compounds were mesomorphic. Lin and co-workers reported on the mesomorphism of 1,3-dialkylimidazolium (61; X = Br, I, PF_6) and 1,3-dialkylbenzimidazolium salts (62; R = C_nH_{2n+1} , Cl, Br, I, PF₆).¹⁵⁶ Mesophases were observed for the chloride and bromide salts but not for the iodide and hexafluorophosphate salts. The mesophase stability range of the 1,3-dialkylimidazolium salts is smaller than that of the 1-alkyl-3methylimidazolium salts. The authors describe the mesophase as bilayered lamellar mesophases L_{α} and L_{β} , the difference being that there is order in the layers of the L_{β} phase, but not in those of the L_{α} phase. A smectic A phase was observed over a broad temperature range for the 1,3-dialkylimidazolium salts with $[CuCl_4]^{2-}$ and $[PdCl_4]^{2-}$ counterions: $[(C_nH_{2n+1})-im]_2[CuCl_4]$ and $[(C_nH_{2n+1})-im]_2[PdCl_4]$.¹⁵⁷ The liquid-crystalline behavior of mixtures of the copper(II) and palladium(II) compounds, as well as mixtures of the metal-containing ionic liquid crystals with the corresponding chloride salts, were investigated. The mixtures have a smaller mesophase stability range than the pure compounds. The mixed anions have a greater influence on the clearing temperatures than on the melting temperatures. The metal-containing ionic liquid crystals show thermal decomposition near the clearing point. For the palladium(II) series, carbene- and dicarbene-imidazolium complexes were generated by the thermal decomposition process. Authors of the same team reported on the thermal behavior of the N-alkylimidazolium salts (**63**, $R = C_n H_{2n+1}$, Cl, BF₄, NO₃).¹⁵⁸ The crystal structure of [C₁₄H₂₉imH][NO₃] was described. The compound forms a lamellar bilayer structure with strongly interdigitated alkyl chains. The nitrate salts with $C_{14}H_{29}$, $C_{16}H_{33}$, and $C_{18}H_{37}$ chains are mesomorphic, exhibiting a smectic A phase. For the chloride salts, a mesophase is observed even for the compound with a C₁₀H₂₉ chain. Moreover, this compound is liquid-crystalline at room temperature. The [BF₄]⁻ salt with C₁₂H₂₅ chain shows a monotropic smectic A phase, whereas the salts with a longer alkyl chain forms an enantiotropic smectic

A phase. When the influence of the anion is compared, it is observed that the chloride salts form the widest temperature range for the mesophase. This is attributed to hydrogen bonding between the chloride anion and the imidazolium cation. The nitrate salt with $C_{12}H_{25}$ chain and the chloride salts with $C_{10}H_{21}$, $C_{12}H_{25}$, and $C_{14}H_{29}$ chain show a lyotropic mesophase in water, acidic water, and THF.



Yoshizawa and co-workers connected the calamitic mesogenic group 4-butoxybiphenyl via a spacer of 8 or 12 methylene groups to a 1-methylimidazolium salt (**64**, n = 8, 12).¹⁵⁹ The compounds with bromide or tetrafluoroborate anions show smectic polymorphism: a smectic E phase was observed below a smectic A phase. The smectic A phase is of the interdigitated type. The introduction of the butyloxy biphenyl group results in the formation of a highly ordered smectic mesophase. Increasing the length of the flexible alkyl spacer improves the stability of the mesophase and the mesophases formed by the bromide salts are slightly more stable than those formed by the tetrafluoroborate salts. The mesophases have a strong tendency to supercool to a glassy state.



Whereas most of the studies on liquid–crystalline imidazolium salts were restricted in the past to compounds forming smectic mesophases, research interests turned recently to imidazolium salts forming columnar mesophases as well. Kato and coworkers observed a hexagonal columnar mesophase in 1-methylimidazolium salts with a tri-alkoxy substituted benzyl group attached to the nitrogen atom, and with $[BF_4]^-$ as the counterion (**65**, R = C₈H₁₇, C₁₂H₂₅).¹⁶⁰ The compounds are liquid–crystalline at room temperature, and the mesophase is stable over a wide temperature range.



Another type of imidazolium salt displaying a columnar mesophase was obtained by N-alkylation of 1-methylimidazole with hexakis(10-bromodecyloxy)triphenylene, followed by anion exchange of Br⁻ by $[BF_4]^-$ (66).¹⁶¹ By covalently attaching an imidazolium group to the triphenylene-mesogen the mesophase was stabilized in comparison to that of triphenylene substituted with only alkoxy chains. Interestingly, addition of 1-hexyl-3-methylimidazolium tetrafluoroborate to the ionic liquid crystals widened the temperature range of the mesophase considerably from 47 to 111 °C to 4–117 °C. However, when 1-hexyl-3-methylimidazolium tetrafluoroborate was mixed with a triphenylene that was substituted by six alkoxy chains, phase separation occurred. So far, columnar mesophases were obtained by anchoring discotic mesogens to an imidazolium salt. In principle, it is also possible to obtain columnar mesophases with the imidazolium group as the rigid core of the liquid crystal.



Imidazolinium salts are closely related to imidazolium salts, but the positive charge is not fully delocalized over the heterocyclic five-ring in the former salts. In contrast to the imidazolium salts, data on the mesomorphic behavior of imidazolinium salts are very scarce. Kraft and co-workers prepared discotic imidazolinium complexes by reaction between a tris(imidazoline) base and aromatic carboxylic acids.¹⁶² The aromatic acids used are 3,4,5-tris-(dodecyloxy)benzoic acid (67), 3,4-bis(dodecyloxy)benzoic acid, 3,4-bis(decyloxy)benzoic acid, and 4-dodecyloxybenzoic acid. The complex structure is formed by self-assembly through hydrogen bonding. The supramolecular liquid crystals exhibit a columnar mesophase, that has very likely a hexagonal symmetry.



3.4. Pyridinium Salts

Thermotropic mesomorphism of pyridinium salts was noticed as early as 1938 by Knight and Shaw.¹⁶³ The authors observed mesophases for N-(n-alkyl)pyridinium chlorides and iodides, with the alkyl chain being $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$ (for the compound with the $C_{12}H_{25}$ chain the bromide salt was prepared as well) (68). The temperature range over which a mesophase was observed decreased in the order chloride > bromide > iodide. The clearing point was much more affected by the choice of the anion than the melting point. The mesophase stability range increased with increasing alkyl chain length. The types of mesophases were not determined, but very likely they observed a smectic A phase in all cases. The mesophase of *N*-(*n*-hexadecyl)pyridinium chloride was later identified as a smectic A phase.¹⁶⁴ Fürst and Dietz found liquid-crystalline character for N-methyl-3-alkylpyridinium, N-methyl-3-alkoxypyridinium, and N-methyl-3-thioalkylpyridinium methosulfates and tosylates.¹⁶⁵



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Chloride salts of protonated 2-alkylpyridines (69) are mesomorphic as well but not the corresponding picrate or picrolinate salts.¹⁶³ For instance, the chloride salt of protonated 2-tridecylpyridine melts at 52 °C and clears at 109 °C, whereas the picrate salt melts to an isotropic liquid at 78 °C. 4-Alkylpyridinium hydrochlorides, hydrobromides, or hydroiodides are not mesomorphic (70), but methylation of the N-atom induces mesomorphism (71).¹⁶⁶



The thermotropic mesomorphism of 4-substituted 1-alkylpyridinium iodides was investigated by Nusselder et al.¹⁶⁷ The authors noticed that a mesophase is present when the substituent in the 1-position of $4-\hat{n}$ -dodecyl-1-alkylpyridinium iodide is a methyl group but not when the methyl was changed into hydrogen, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *n*-hexyl, 3-hydroxypropyl, or 2-methoxyethyl. Given the fact that the N-alkylpyridinium (1-alkylpyridinium) compounds exhibit a mesophase for very long chain lengths (see further), it can be predicted that the 4-substituted 1-alkylpyridinium iodides can be made liquid-crystalline by inserting a long alkyl chain in the 1-position. A very strong dependence of the clearing point on the alkyl chain length was observed for the 4-alkyl-1-methylpyridinium iodides, whereas the melting point remained more or less constant. For instance, when a dodecyl chain was replaced by a tetradecyl chain, the melting point increased from 113 to 115 °C, but at the same time the clearing point increased from 148 to 208 °C! A study of the effect of branching of the alkyl chain showed that the mesophase is more destabilized when the branching point is placed closer to the point of attachment on the pyridine ring. When the branching point is placed further away from the pyridinium ring, less destabilization of the mesophase occurs. In all cases where the mesophase could be identified with certainty, a smectic A phase was found. For the 1-methyl-4alkoxycarbonylpyridinium iodides thermochromism was observed but not for the 1-methyl-4-alkylpyridinium iodides. This is attributed to the fact that the presence of an electron-withdrawing group in conjugation with the pyridinium ring shifts the chargetransfer band toward the visible spectral region.

The *N*-(*n*-alkyl)-4-methylpyridinium bromides (72) show a smectic A phase for alkyl chains with 16 or more carbon atoms.¹⁶⁸ The melting point increases only slightly with increasing alkyl chain length, but a very sharp increase in the clearing point with increasing chain length was observed. Microscopy studies showed that these compounds have a very strong tendency for homeotropic alignment. The model proposed for the molecules in the smectic A phase is one in which the molecules within one layer are oriented on average perpendicularly to the layer plane in alternate head-to-tail fashion.¹⁶⁹ The bromide ions are positioned in such a way that they are sandwiched between the pyridinium rings of neighboring molecules. There is thus an interdigitation of the bromide ions and pyridinium headgroups of neighboring layers, probably accompanied by some interdigitation of the alkyl chains in the neighboring layers. When the methyl group in the 4-position of the pyridinium ring of the N-alkylpyridinium salts was replaced by a cyano group (73), the melting point increases and the mesophase stability range decreased.¹⁷⁰ A partially bilayered smectic B phase was found for N-(*n*-hexadecyl)-4-cyanopyridinium iodide.¹⁷¹ The strong dipole moment of the cyano group is thus responsible for the formation of an ordered smectic B phase. Recall that N-(n-hexadecyl)-4-methylpyridinium iodide exhibits a smectic A phase. *N*-(*n*-hexadecyl)-4-cyanopyridinium iodide also shows

very distinct thermochromic properties: yellow in the crystalline state and red in the mesophase. On the other hand, no thermochromism is observed for N-(nhexadecvl)-4-methylpyridinium iodide. This indicates that the cyano group is necessary to promote thermochromism. The effect is probably caused by charge transfer from the iodide ions to the positively charged pyridinium ring. In a structural model for N-(nhexadecyl)-4-cyanopyridinium iodide, the authors propose a pairing of the iodide ions. The N-alkylpyridinium hydrogen sulfates are thermotropic liquid crystals, but the mesophase behavior has not been investigated in detail yet.¹⁷² Interestingly, these compounds form lyotropic mesophases in concentrated sulfuric acid, and the phase sequence as a function of the concentration of the pyridinium salt is similar to the sequence found for cationic surfactants in aqueous solution. 1-Citronellylpyridinium bromide (74) is a chiral ionic liquid crystal, but is exhibits an achiral smectic phase, just as 1-citronellyl-3-methylimidazolium bromide.¹⁵³



The mesomorphism of the *N*-alkylpyridinium alkyl sulfates (**75**) has been thoroughly investigated.^{173,174} The influence of a combined change of the chain length of both the *N*-alkyl group and of the alkyl group of the alkyl sulfate anion has been studied. Although a large variation in chain lengths was investigated, this variation is not reflected in a large variation in transition temperatures. All the compounds exhibit a single smectic A phase.



In several mesomorphic pyridinium salts, the pyridinium ring is substituted by a second ring, which can either be aromatic or aliphatic. Bazuin and co-workers investigated the mesophase behavior of the N-(n-alkyl)-4-tolylpyridinium bromides (**76**) and compared these compounds with N-(n-alkyl)-4-methylpyridinium bromides.¹⁶⁸ Interestingly, these compounds exhibit a crystal G phase (smectic G phase). For the compounds with a longer alkyl chain (C₁₆H₃₃ and C₂₂H₄₅), a smectic A phase was observed between the crystal G phase and the isotropic liquid. The fact that the isotropization temperatures are very similar for N-(n-alkyl)-4-tolylpyridinium bro-

mides and *N*-(*n*-alkyl)-4-methylpyridinium bromides (for the same alkyl chain length) indicates that ionic forces are primarily responsible for maintaining the layer structure of these compounds to high temperatures. On the other hand, the elongation of the ionic headgroup leads to the formation of an ordered smectic phase at intermediate temperatures. Both an ordered smectic phase and a smectic A phase were observed for 4-(phenol)-*N*-(*n*-octadecyl)pyridinium triflate (**77**).¹⁷⁵ This material was processed to highly ordered noncentrosymmetric Langmuir–Blodgett films, which are transparent in the visible spectral region, and which shows nonlinear optical properties (NLO properties). The value of first-order hyperpolarizability is rather high.



Haramoto and co-workers prepared mesomorphic *N*-alkylpyridinium salts that are substituted in the 4-position by either a 1,3-dioxane ring (78),¹⁷⁶⁻¹⁸⁰ a 1,3-dithiane ring (79),¹⁸¹ or a 1,3-oxathiane ring (80).^{178,182} The most remarkable property of these ionic liquid crystals is the wide temperature range over which the smectic A phase is stable. Many of the compounds are also liquid-crystalline at temperatures far below room temperature. Moreover, the compounds have a large dielectric constant perpendicular to the molecular axis.¹⁷⁷ This effect is attributed to the spatial separation of cation and anion in the ionic liquid crystal molecule. The compounds with a 1,3-dithiane ring have higher transition temperatures than the corresponding compounds with a 1,3-dioxane ring. It was found that compounds with a terminal double bond in the alkyl chain have a lower clearing point than molecules which do not have this structural feature.^{181,180} This is in agreement with the observation by other authors that the mesophase-to-isotropic liquid transition is reduced by a terminal double bond in the chain.^{183,184} The layer spacing of the smectic A phase depends on the type of counterion.¹⁷⁹ For a series of compounds with halide counterions, the layer spacing decreases with increasing size of the halide ion (the largest spacing is found for chloride salts, the smallest spacing for iodide salts). The larger iodide ions make the lateral



interactions between the liquid crystal molecules weaker, so that the interdigitation of the alkyl chains is more pronounced.

A chiral pyridinium compound with a 1,3-dioxane (81) ring was mixed with a ferroelectric liquid crystal, and spontaneous polarizations, response times and dielectric constants were measured.¹⁸⁵ Again, it was noticed that the dielectric constant was large perpendicular to the molecular axis. Haristoy and Tsiourvas investigated the liquid-crystalline properties of *N*-alkylpyridinium salts with an oxadiazole group in the 4-position of the pyridine ring (82).^{186,187} A smectic A phase was formed. The compounds exhibit thermochromism: their color changes from pale yellow at room temperature to bright red in the mesophase. The color change is attributed to the formation of a charge-transfer complex in the mesophase. The effect is reversible. A problem of the salts with bromide counterions is their relatively low thermal stability. By replacing the bromide ion by alkyl sulfate counterions, the clearing point was depressed and no thermal degradation was observed.¹⁸⁷ When bis(2ethylhexyl)sulfosuccinate was chosen as the counterion, no mesophase was observed; the compound is a room temperature ionic liquid. However, neither the compounds with alkyl sulfate nor with bis(2-ethylhexyl)sulfosuccinate showed thermochromic behavior. This gives further evidence for attributing the origin of the thermochromism to the formation of a charge-transfer complex.



The thermal behavior of trans-N-alkyl-4-nitro-4'stilbazolium, trans-N-alkyl-4-cyano-4'-stilbazolium, and *trans-N*-alkyl-4-methoxy-4'-stilbazolium salts with chloride, bromide, and iodide counterions has been described by Kosaka et al. $(83-85, X = Cl, Br, I)^{188}$ A smectic A phase was observed for the trans-Nalkyl-4-nitro-4'-stilbazolium salts, whereas the thermal stability of the 4-cyano and 4-methoxy substituted compounds was too low for a detailed study of their thermal behavior. The stability range of the smectic A phase of the trans-N-alkyl-4-nitro-4'stilbazolium salts was found to be dependent on the halide anion and decreases in the order $Cl^- > Br^- >$ I⁻. The temperature range of the mesophase thus decreases with increasing size of the anion. The authors performed miscibility studies of their stilbazolium compounds with different Schiff base mesogens. A 1:1 mixture between trans-N-hexyl-4-nitro-4'-stilbazolium bromide and the Schiff base 4-hexyloxy-*N*-(9-methyl-2-carbazolylemethylene) aniline exhibits a smectic A phase, although the two components are not mesomorphic themselves. The mesophase induction is due to an electron-donor acceptor interaction between the electron-deficient nitro-stilbazolium group and the electron-rich carbazolyl group.



The trans-N-alkyl-4-nitro-4'-stilbazolium salts (86) have been used to induce a smectic A phase in nematogenic liquid-crystalline side-chain polymers.¹⁸⁹ Binnemans and co-workers investigated a series of ionic liquid crystals with the hemicyanine (aminostryrylpyridinium) structural unit and with a long alkyl chain on the N-atom on the pyridine ring (87).¹⁹⁰ A smectic A phase was observed for compounds with bromide counterions. The transition temperatures are not strongly influenced by the alkyl chain length. When the bromide ion was replaced by iodide, the corresponding compound did not exhibit a mesophase.¹⁹¹ These findings are in contrast with earlier work by other authors.¹⁹² The nonlinear properties of the stilbazolium salts with bromide and with tetrakis β -diketonate counterions have been investigated.193,194



Quaternized cholesteryl isonicotinates with tosylate counterions (88) exhibit an enantiotropic chiral nematic phase (cholesteric phase), whereas the cholesteryl isonicotinates themselves show a monotropic chiral nematic phase.¹⁹⁵ The compounds decompose in the mesophase before the clearing point is reached.



In a series of *N*-alkylpyridinium halides which are ω -substituted by a 4-methoxybiphenyloxy mesogenic group (**89**), three types of smectic phases were observed: smectic A, smectic B, and crystal E.¹⁹⁶ For identification of these mesophases, one has to rely on the wide angle part of the X-ray diffractogram

because the small angle part only gives information on the interlayer distance not on the arrangement of the molecules within the layer. The smectic A phase is characterized by a single diffuse band in the wide-angle region of the X-ray diffractograms. For the smectic B phase, one rather narrow Bragg peak is observed in the wide-angle region. This reflection points to a two-dimensional ordering of the molecules within the layers and can be indexed as the (100) reflection of a two-dimensional lattice. The crystal E phase shows two sharp reflections in the wide-angle region. These reflections can be indexed as the (110)and (200) reflections from a two-dimensional centered rectangular lattice. The structure of these smectic phases consist of single layers of upright molecules laterally arranged head to tail. The alkyl chains are intimately interdigitated. A study of similar compounds with an ethyl group on the pyridinium ring shows that mesomorphism is present for the 2-ethylpyridinium and 4-ethylpyridinium compounds but not for the 3-ethylpyridinium compounds.¹⁹⁷ The ethyl substitution of the pyridinium ring affects the packing of the molecules because the ethyl group is located within the ionic moiety which controls the stacking of the molecules. In a study by Lattermann and co-workers, the methoxy group on the biphenyl group of the ω -substituted N-alkylpyridinium salts was replaced by a cyano group or by a long alkyl chain (**90**; $R_1 = CN$, OC_3H_7 , $OC_{10}H_{21}$; $R_2 = H$, 2-ethyl, 4-ethyl, 3,5-dimethyl; m = 6, 10).¹⁹⁸ The length of the spacer between the pyridinium ring and the biphenyl group was varied, and the pyridinium ring was substituted in the 2-, 4- and in the 3,5-position. The most stable mesophases were observed for the unsubstituted pyridinium rings. For the 2-ethyl, and 4-ethyl substituted pyridinium rings, mesomorphism is only observed if a decyl chain is present on both sides of the biphenyl core (i.e., a decyl terminal chain and a decyl spacer). Depending on the substitution pattern of the pyridinium ring in the case of the compounds with two decyl chains, different smectic phases were observed (smectic A, smectic B, smectic C), and also smectic polymorphism was sometimes present in the mesophase. No mesomorphism was observed for the compounds with a 3,5-dimethyl substituted pyridinium ring. The compound with a cyanobiphenyl group in the ω -position of the alkyl chains and an unsubstituted pyridinium ring showed a monotropic smectic A phase when the crystalline solid was considered, but this smectic A phase could be supercooled to a glassy state, which generated the smectic A phase again upon heating.



A 2,6-substituted pyridinium triflate with partially fluorinated alkyl chains was reported to be meso-



Figure 9. Schematic representation of the thermotropic polymorphism of the N-alkylpyridinium tetrachlorocuprate(II) compounds. The arrows mean increasing temperatures, while d represents the layer spacing. Reprinted with permission from ref 203. Copyright 2001 American Chemical Society.

morphic (**91**).¹⁹⁹ Hessel et al. described the mesomorphism of dipolar amphiphiles with two pyridinium headgroups fixed to a biphenylene core (**92**; m = 11, 12, 16).²⁰⁰ The pyridinium ring has been connected via a flexible spacer to hexaalkoxytriphenylene molecules (**93**; n = 3, 4, 5; $R = C_4H_9$, C_5H_{11} , C_6H_{13}).²⁰¹ The compounds were found to exhibit a columnar mesophase. While increase of the chain length of the alkyl chains on the triphenylene core has a stabilizing effect on the mesophase, the reverse is true for the spacer length between the triphenylene core and the pyridinium ring.



The simple inorganic anions in *N*-alkylpyridinium salts can also be replaced by tetrachlorometalate complexes, $[MCl_4]^{2-}$, where the metal M = Co, Ni, Cu, Zn, Pd, Cd.^{137,202-204} Because of the +2 charge of the tetrachlorometalate anion, two *N*-alkylpyridinium moieties are present for each $[MCl_4]^{2-}$ groups. The coordination sphere of the metal center is close to square-planar in the tetrachloropalladate(II) complexes, whereas it is tetrahedral for the other metals.

These compounds exhibit a mesophase, provided that the N-alkyl chain is long enough. In practice, a mesophase is observed for compounds with a dodecyl or a longer chain. In the case of the tetrachloropalladate(II) complexes, at least a tetradecyl chain is necessary to induce a mesophase. For M = Co, Ni, Zn, Cd, the mesophase was identified as a smectic A phase. A detailed study of the [ZnCl₄]²⁻ and [CdCl₄]²⁻ compounds revealed that the smectic A phase is in fact a partially bilayered smectic A phase.²⁰⁴ A striking feature of these compounds is that when the compound is heated a marked increase of the dspacing of the layers is observed at the melting point, i.e., the interlayer distance is larger in the mesophase than in the crystalline state. This increase in dspacing is attributed to a significant relaxation (with concurrent disordering) of the interdigitated arrangement of the alkyl chains in the crystal. The *d*-spacing of the smectic A phase decreases with increasing temperature, as expected. The crystalline state of the tetrachloropalladate(II) compounds is transformed at the melting point to an ordered smectic phase (identified as a crystal E phase), while at more elevated temperatures a partially bilayered smectic A phase is observed.²⁰² Moreover, solid state polymorphism is observed as well for these compounds. The transition temperatures are only slightly influenced by the alkyl chain length. The most interesting mesophase behavior is observed for the tetrachlorocuprate(II) salts (Figure 9).²⁰³ The $[CuCl_4]^{2-}$ derivatives with an alkyl chain with 10 or less carbon atoms are nonmesomorphic, but they are room temperature ionic liquids. The compound with a $C_{11}H_{23}$ chain is a solid at room temperature and melts upon heating directly to an isotropic liquid. All the compounds with an alkyl chain of 12 or more carbon atoms are mesomorphic, and both the melting and the clearing point increase with increasing chain length. The increase is more pronounced for the clearing point than for the melting point. The compounds with a $C_{12}H_{25}$, C₁₃H₂₇, and C₁₄H₂₉ chain exhibit a hexagonal columnar mesophase. The derivatives with C₁₆H₃₃, C₁₇H₃₅, and $C_{18}H_{37}$ chain have a smectic A phase. The compound with a C₁₅H₃₁ chain exhibits a cubic

mesophase between the crystalline state and a (partially bilayered) smectic A phase. Later work showed that the space group symmetry this thermotropic cubic phase is $Ia\bar{3}d$.²⁰⁵ This cubic phase is only observed for the derivative with the pentadecyl chain not for the derivatives with shorter or longer chains. Because the cubic phase is detected for a compound with an alkyl chain containing an odd number of carbon atoms, it surprising that it was not overlooked in the study of the homologous series of tetrachlorocuprate(II) compounds; often only the members with an even number of carbon atoms in the alkyl chain are made (due to the much higher price of the precursors with an odd number of carbon atoms). Besides the occurrence of a thermotropic cubic phase for the compound with C₁₅H₃₁ chain, the mesomorphism of the tetrachlorocuprate(II) derivatives is for other reasons uncommon as well. In a homologous series that exhibits both a columnar and a smectic mesophase, the columnar mesophase is in general observed for the homologous compounds with the longer chain lengths, whereas for the tetrachlorocuprate(II) derivatives the opposite is true. Second, there are very few examples known of single-tail amphiphiles exhibiting thermotropic columnar phases. Typical compounds that show a columnar mesophase have a large number of alkyl chains. A disadvantage of the tetrachlorocuprate(II) derivatives is that they are not stable in water; they decompose when these are dissolved in water.

The presence of a mesophase in the *N*-alkylpyridinium salts with tetrahalometalate anions is not restricted to the chloro-compounds; also the corresponding bromo-compounds display mesomorphism as well, and the mesophase behavior is often very comparable. For instance, like the tetrachlorocuprate(II) compound with pentadecyl chain, the tetrabromocuprate(II) derivative shows a thermotropic cubic mesophase.²⁰⁵ When the mesophase behavior of the tetrabromopalladate(II) compounds is compared with that of the tetrachloropalladate(II) complexes, one notices that the chloro derivatives show a crystal E phase between the crystalline solid and the smectic A phase, whereas this crystal E phase is absent in the series of bromo complexes.²⁰² The presence of the ordered smectic phase is attributed to the stronger (C-)H····Cl hydrogen bonds in comparison to the (C-)H···Br hydrogen bonds. The fact that the mesophase behavior depends on the type of metal indicates that the metal itself seems to play a subtle role in the stabilization of mesophases. In contrast to the tetrachloropalladate(II) and tetrabromopalladate(II) complexes, the tetraiodopalladate complexes do not show a mesophase at all.²⁰⁶ The related compounds with [Pd₂I₆]²⁻ anions were not mesomorphic either. The absence of (smectogenic) mesomorphism for the iodo compounds is explained as being due to the weakness of the (C-)H····I hydrogen bonds in the structure. Although the N,N'dodecamethylene-bis(pyridinium) salts with halometalate anions are inorganic-organic hybrid materials with a rich structural chemistry, they are not mesomorphic.^{207,208} The same conclusion holds for the *N*-alkylpyridinium salts which a COOH group in the ω -position of the alkyl chain.²⁰⁹

Taubert described the use of an ionic liquid crystal as a template to synthesize copper(I) chloride nanoplatelets.²¹⁰ N-Dodecylpyridinium tetrachlorocuprate(II) was mixed with the hydrophobic reducing agent 6-O-palmitoyl ascorbic acid (94), and the CuCl platelets were formed by heating of the mixture. The platelets formed in the mesophase at 85 °C are relatively large and interconnected, whereas smaller platelets without permanent junction were formed in the isotropic liquid. The fact that CuCl platelets are not only formed in the mesophase, but also in the isotropic liquid indicates that some ordering of the solvent must exist in the isotropic phase (a platelet morphology is uncommon for CuCl). Some authors consider ionic liquids as ordered solvents, even if the ionic liquid does not form a mesophase.^{142,211-213}



Kresse and co-workers built a bridge between the field of ionic liquid crystals and hydrogen-bonded liquid crystals.^{214–217} In their studies, Kresse et al. investigated hydrogen-bonded associates formed between 1-*n*-heptyl-4-(4-pyridyl)pyridinium bromide as an ionic hydrogen-bond acceptor and different kinds of hydrogen donors. Binary phase diagrams were constructed from data obtained by the contact method. In such a phase diagram, a thermodynamically stable 1:1 hydrogen-bonded associate is indicated by two eutectic points. The hydrogen-bond acceptor 1-nheptyl-4-(4-pyridyl)pyridinium bromide (95) is a crystalline solid that melts at 127 °C to an isotropic liquid. When this compound is mixed with the nematogen 4-*n*-butyloxybenzoic acid, a smectic A phase is induced (due to the formation of a hydrogen-bonded complex 96).²¹⁴ This smectic phase has a maximum stability when the molar fraction of the pyridinium salt is 0.4. The maximum clearing temperature is thus not at a 1:1 ratio of donor and acceptor. Even small quantities of *n*-heptyl-4-(4-pyridyl)pyridinium bromide are sufficient to suppress the nematic phase of 4-n-butyloxybenzoic acid. The mesophase of the ionic associate formed with *n*-heptyl-4-(4-pyridyl)pyridinium bromide as the acceptor is not completely miscible with the mesophase formed by the nonionic hydrogen-bond acceptor 4-(4-n-hexyloxyphenyl)pyridine, although the hydrogen-bond donors both exhibit the same mesophase (smectic A) and both compounds have a very similar structure. The broad miscibility gap points to a strong incompatibility between the ionic and the nonionic liquid-crystalline phases. In the phase diagram with the partially fluorinated hydrogen-bond donor 4-n-1H,1H-perfluorobutyloxybenzoic acid, the smectic A mesophases is stabilized in comparison with that of the nonfluorinated acid, and the maximum mesophase stability is now found for the 1:1 ratio. Whereas trans-4-n-octylcyclohexane-1-carboxylic acid shows a smectic B phase and a nematic phase, in the mixtures with n-heptyl-4-(4pyridyl)pyridinium bromide these phases are not stabilized and at molar fractions of n-heptyl-4-(4pyridyl)pyridinium bromide higher than about 0.10 only a smectic A phase was detected.²¹⁵ No mesophases were detected in the system with 1.12dodecanedicarboxylic acid as the hydrogen-bond donor.²¹⁵ A smectic A phase with a very high stability was observed for an equimolar mixture of *n*-heptyl-4-(4-pyridyl)pyridinium bromide and the swallowtailed carboxylic acid 4-[2,2-bis(tetradecyloxycarbonyl)ethenvllbenzoic acid.²¹⁵ Mixtures with 4-(3,4,5-tri-ndodecyloxybenzoyloxy)benzoic acid reveal the presence of a smectic A phase at low donor concentration and a columnar phase at high donor concentrations.²¹⁷ On the other hand, in the binary phase diagram with 3,4-di-n-heptyloxybenzoic acid, only a smectic A phase is present. Not only can carboxylic acids be used as hydrogen-bond donor but also phenols.²¹⁶ Here again, smectic A phases are induced by associate formation with *n*-heptyl-4-(4-pyridyl)pyridinium bromide, although the stability of the smectic phase is lower than in the case in which carboxylic acids are used as donor molecules. Mixtures of pyridine and octylphosphoric acid form a room temperature smectic phase for pyridine to octylphosphoric acid ratios from 0.2 to 0.8^{218}



3.5. Viologens

Viologens is a trivial name for 1,1'-disubstituted-4.4'-bipyridinium salts.²¹⁹ These compounds are used as herbicides, but they are also used as electrochromic and thermochromic materials and as active components in molecular electronics. Viologens with long alkyl chains are liquid-crystalline and the mesophase behavior depends on the type of anion.²²⁰⁻²²⁵ 1,1'-Diheptyl-4,4'-bipyridinium dibromide and 1,1'-dioctyl-4,4'-bipyridinium dibromide decompose without melting, whereas the corresponding bis(triflimide) salts exhibit a smectic A phase (97).^{224,226} This work was extended to other chain lengths.²²⁵ 1,1'-Dipentyl-4,4'-bipyridinium bis(triflimide) is a ionic liquid crystal at room temperature (smectic A phase), but both 1,1'-dibutyl-4,4'-bipyridinium bis(triflimide) and 1,1'-dihexyl-4,4'-bipyridinium bis(triflimide) have melting points well above room temperature. No mesophase was observed for the tetrafluoroborate salts. By replacement of the alkyl chain by an oligoethyleneoxide chain, compounds with a large mesophase stability range could be obtained.^{220,221} 1,1'-Di(3,6,9-trioxatridecyl)-4,4'-bipyridinium diiodide (98) is liquid-crystalline between 63 and 216 °C.²²⁰ On the other hand, 1,1'-di(3,6,9trioxatridecyl)-4,4'-bipyridinium bis(tetrafluoroborate) and 1,1'-di(3,6,9-trioxatridecyl)-4,4'-bipyridinium ditosylate are not mesomorphic, but they are

room temperature ionic liquids.²²² The 1,1'-diphenyl-4,4'-bipyridinium dialkylbenzenesulfonates exhibit a smectic A phase at high temperatures.²²³



The liquid-crystalline viologens with oligoethyleneoxide chains have been used to construct digital memories that are not influenced by electromagnetic noise.²²⁷ It was observed that the viologens in the liquid-crystalline state are electric semiconductors and that they could be transformed into a state with a much higher electric conductivity by applying a voltage above a certain threshold over two ITO electrodes in a sandwich cell filled with the liquid crystal.²²⁰ An increase in electric conductivity by a factor of 10⁴ was observed by applying a voltage of 30 V over the electrodes. The liquid-crystalline viologen kept this high electric conductivity, even when the voltage was no longer applied. In the memory device, the writing step consists of transforming the liquid-crystalline viologen from a state of low electric conductivity to a state of high electric conductivity by applying a voltage pulse. The device detects in the reading step by application of a low voltage over the cell whether the liquid-crystalline viologen is in a state of low conductivity or in a state of high conductivity (via measurement of the electric conductivity).

Structurally related to the viologens are compounds in which another group is inserted between the two pyridine rings of the 4,4'-dipyridine. For instance, Yousif et al. inserted an alkene,²²⁸ an azine,²²⁹ or a thiadiazole group.²³⁰

3.6. Pyrylium and Thiopyrylium Salts

Saeva et al. reported that pyrylium salt 99 shows smectic mesomorphism between 117 and 139.5 °C.231 A smectic-to-smectic phase transition was observed at 137 °C. However, the smectic mesophases were not further investigated. Gionis and co-workers reinvestigated this compound.²³² They found slightly different transition temperatures but did not mention smectic polymorphism. The mesophase was identified as a smectic A phase.²³³ These authors made a systematic study of the mesomorphism of 2,6-diarylpyrylium (100-105) and 2,6-diarylthiopyrylium compounds (106, 107), symmetrically substituted with one or two alkoxy chains or with one alkyl chain on the phenyl ring.^{232,233} In all cases, the anion was perchlorate. The pyrylium salts with an alkyl chain on the para-position of the phenyl ring are mesomorphic for alkyl chains with eight or more carbon atoms. On the other hand, the corresponding thiopyrylium salts have a mesophase only for alkyl chains with 12 or more carbon atoms. The pyrylium and thiopyrylium salts with an alkoxy chain in the para-position of the phenyl ring are mesomorphic as long as the alkoxy chain contains nine or more carbon atoms.^{234,235} The meta-substituted compounds with an alkoxy chain show mesomorphism for chain lengths of eight or more carbon atoms. None of the orthosubstituted compounds is mesomorphic. Of the pyrylium and thiopyrylium salts with two alkoxy chains on each of the two phenyl rings, those with the 2,4substitution pattern are non-mesomorphic, while those with a 2,5-substitution pattern are mesomorphic.²³² In general, the melting points (crystal-tomesophase transitions) are lower for the thiopyrylium salts than for the pyrylium salts with the same substituents. The melting points of the meta-substituted compounds are lower than those of the parasubstituted compounds. The temperature range of the mesophase is larger for the alkoxy derivatives than for the alkyl derivatives. Disubstitution on a phenyl ring leads to lower transition temperatures. The pyrylium salts with alkoxy chains in the 2,5 positions and with perchlorate anions are even at room temperature liquid-crystalline.²³² No data are available for the corresponding thiopyrylium salts or for salts with counteranions other than perchlorate. The pyrylium salts with one alkoxy chain on the phenyl ring often show polymorphism, both in the solid state and in the mesophase. Although not all these phases have been studied in detail yet, there is enough evidence that the smectic phase at the highest temperature (i.e., the one which is formed first when the isotropic liquid is cooled) is a smectic A phase.²³³ The entropy change for the isotropic-tosmectic A phase is remarkably low (5 J mol⁻¹ K⁻¹) in comparison to that observed for most other liquid crystals with a smectic A phase $(12-30 \text{ J mol}^{-1} \text{ K}^{-1})$. This can point to a more or less complete melting of the aliphatic chains in the smectic A phase of the pyrylium salts, while in most other compounds there is still a high probability to have the all-trans conformation for the aliphatic chains. A distinct increase in *d*-spacing of the smectic layers is observed when the temperature decreases.





Veber and co-workers investigated the pyrylium salts with the phenyl rings substituted by two alkoxy chains in the 3- and 4-positions and with tetrafluoroborate anions.^{236,237} These compounds with four alkoxy chains in total show a hexagonal columnar phase for alkoxy chains with eight or more carbon atoms. A rich polymorphism was observed in the crystalline state. These investigations were extended to compounds with six alkoxy chains, being the 2,4,6triarylpyrylium tetrafluoroborates (108).^{238,239} The salts show a hexagonal columnar phase (Col_h) over a wide temperature range. The compounds with six OC₅H₁₁, OC₈H₁₇, or OC₁₂H₂₅ are liquid-crystalline at room temperature. Whereas the compounds with OCH_3 substituents are not mesomorphic, those with OC_2H_5 and OC_3H_7 chains are. These latter two compounds display a hexagonal columnar phase (space group P6/mmm), with a coherence length of the columnar stacking of about 400 Å. For the existence of a hexagonal columnar mesophase, it is necessary that the neighboring columns are discorrelated. Disordered alkoxy chains are important for the breakdown of this correlation in classic discotic liquid crystals. This is probably not possible for alkoxy chains as short as ethoxy and propoxy chains. It is assumed that the BF_4^- anions play a role in the mesophase formation. From X-ray data, it was derived that the BF_4^- anions are spatially disordered but still located close to the aromatic cores of the pyrylium salts. ¹⁹F NMR measurements of the compounds with OC_4H_9 , OC_5H_{11} , OC_8H_{17} , and $OC_{12}H_{25}$ (measurement on the compounds with OC_2H_5 and OC₃H₇ chains was not possible because of low thermal stability) showed that the BF_4^- anions undergo several types of motion.²³⁹ At low temperatures, the BF₄⁻ anions are in a fixed position close to the oxygen atom of the pyrylium ring. At increasing temperatures, the BF₄⁻ anions start to undergo fast reorientations. However, the anions are still trapped in a fixed position at this stage. The rotations can be around the column axis and/or a parallel axis going through their own centers. The rotation of the anions becomes more and more spherical as the temperature increases. Then, the BF₄⁻ anions may undergo translational diffusion and can even migrate from the core to the aliphatic region. At high temperatures, the spherical reorientation motion of the tetrafluoroborate anions is complete. It is argued that the onset of this motion is responsible for discorrelating neighboring columns and for the induction of the hexagonal columnar mesophase in the compounds with OC₂H₅ and OC₃H₇ chains. In the columnar mesophase, the intercolumnar distances can be tuned by the length of the alkyl chains in the paraffinic continuum.



108

The photophysical properties of 2,4,6-triaryl pyrylium salts have been investigated.²⁴⁰⁻²⁴² Polarized absorption and fluorescence spectra could be measured on oriented films of the pyrylium salts in the mesophase.²⁴² Oriented thin films were obtained by shearing. In this process a few milligrams of the compound was spread on a heated quartz slide. The absorbance perpendicularly to the shearing direction was found to be larger than parallel to the shearing direction, up to a factor four. The pyrylium salts thus show a pronounced dichroism. The shearing direction corresponds to the direction of the column axis. The absorption spectra are quite insensitive to disorder in the column. On the other hand, the Stokes shift in the fluorescence spectra depends on the order in the columns. The Stokes shift is smaller for ordered columns than for disordered ones. The shift is independent of the column length.

The compounds show a strong tendency for selfassociation in *n*-heptane, and the absorption and fluorescence spectra depend on the size of the aggregates.²⁴³ The pyrylium salts behave like amphiphilic compounds, and it is possible to prepare Langmuir–Blodgett films of these compounds.^{244,245} The molecular arrangement in the Langmuir– Blodgett films corresponds to a discotic nematic order. Veber and Berruyer prepared dimeric 2,4,6triarylpyrylium tetrafluoroborates with flexible and rigid linking groups (**109**, **110**).²⁴⁶ All these compounds show a hexagonal columnar phase.



3.7. Dithiolium Salts

The thermal behavior of symmetrically substituted 3,5-diaryl-1,2-dithiolium salts was first investigated by Veber and co-workers.^{234–236,247–249} These compounds have either one or two alkoxy chains on each of the aryl rings, thus two or four alkoxy chains in total. The mesomorphic properties depend on the number of alkyl chains per cation. The compounds with two chains per cation exhibit a smectic A phase, whereas the compounds with four chains per cation show a hexagonal columnar phase.²³⁵ The liquid–crystalline dithiolium salts can be used to prepare Langmuir–Blodgett films.²⁵⁰

For the compounds with two alkoxy chains, the position on the alkoxy chain is of importance for the liquid-crystallinity: a mesophase is observed only for the para-substituted compounds (111) not for the meta- or ortho-substituted ones.²³⁴ The length of the alkoxy chain is important too since a smectic A phase could not be observed for compounds with an alkoxy chain of less than nine carbon atoms. The thermal stability of the dithiolium compounds with perchlorate anions is larger than that of the corresponding pyrylium salts but less than that of the thiopyrylium derivatives. On the other hand, the temperature of isotropization (SmA \rightarrow I transition) is higher for the dithiolium salts than for the pyrylium and thiopyrylium salts. In the compounds with the decyloxy and the dodecyloxy chains in the para-position, the melting point increases in the order $Cl^- < PF_6^- <$ ClO_4^- , whereas for the clearing point the order depends on the chain length.



Mesomorphism is observed for the cations with four alkoxy chains if the chain contains eight or more carbon atoms.⁴ The compounds show a rich polymorphism in the solid state. Both the melting and the clearing points are higher for the compounds with $[ClO_4]^-$ anions than for those with $[BF_4]^-$ anions. As mentioned above, the mesophase was identified as a hexagonal columnar phase (Col_h). DSC measurements showed that the compounds decompose at temperatures higher than the point of isotropization.

Veber and co-workers synthesized two series of nonsymmetrically substituted 3,5-diaryl-1,2-dithiolium salts (**112–121**).²⁴⁷ The first series consists of compounds with two alkoxy chains on one aryl group, whereas the other aryl group is unsubstituted. The second series consists of dithiolium salts with three alkoxy chains. These compounds were prepared to determine whether they show a smectic A phase, a hexagonal columnar phase, or an intermediate lamello-columnar phase. Some of the compounds are non-mesomorphic, while others exhibit a smectic A phase, but none have a hexagonal columnar phase or a lamello-columnar phase. X-ray diffraction indicates that the smectic A phase has a very weak local order in the stacking of the rigid cores. On the other hand, the aliphatic chains are more disordered in monolayer smectic A phases formed by classic non-



ionic liquid crystals. The transition temperatures of the nonsymmetrical dithiolium salts with tetrafluoroborate counterions are lower than those of the symmetrical dithiolium salts. The nonsymmetrically substituted dithiolium salts have a stronger tendency to align homeotropically than the symmetrically substituted salts. The authors proposal different structural models for the organization of the molecules in the mesophase, but on the basis of the available experimental data it was not possible to decide which model describes the actual situation most accurately. From X-ray data, it was determined that the $[BF_4]^-$ anions are disordered and located close to the rigid cores of the cations.

The dithiolium salts bearing a branched alkoxy chain (122) show a very interesting mesophase behavior.²⁴⁹ The compounds were obtained as racemic mixtures. They do not exhibit lamellar phases but only columnar mesophases, although these compounds have a rodlike shape. The supramolecular organization is close to that of cylindrical inverted micelles. The heteroaromatic cores and the anions are inside the columns, surrounded by aliphatic chains without any positional order along the column axis. At low temperatures, the columns are stacked in either a rectangular 2D lattice (rectangular columnar phase, Col_r) or a hexagonal 2D lattice (hexagonal columnar phase, Col_b). At higher temperatures, the columnar mesophases are transformed into a nematic columnar phase (N_{col}) . In this phase, the columns are almost parallel without long-range lateral positional correlations. The ionic interactions in the columns stabilize the columns, so that the 2D lattice can melt without complete destruction of the columns. The compounds are one of the few examples in which thermotropic liquid crystals exhibit a nematic columnar phase. This is also a good example of a case in which the ionic character of a compound influences the mesophase behavior. Upon cooling of the sample from the isotropic liquid, first the N_{col} phase is formed. Then the transition to the hexagonal lattice occurs (Col_h phase), followed by transition a rectangular lattice with Cmmm symmetry (Col, phase). Finally, crystallization to a metastable crystalline phase takes place.



3.8. Vinamidinium Salts

Vinamidinium (or 1,5-diazapentadienium) salts have a delocalized acyclic π -system. Only very few examples of mesomorphic vinamidinium salts have been reported in the literature. Zinsou et al. compared the thermal behavior of vinamidinium salts with that of the corresponding vinamidines.^{251,252} Whereas vinamidinium salts with two and four alkyl chains are not mesomorphic, a vinamidinium triflate salt with six alkyl chains exhibited a hexagonal columnar mesophase (**123–126**). The thermal stability of the compound was not very high, and decomposition occurred in the isotropic state. The choice of the anion is important because no mesomorphism was observed when the triflate anion was replaced by tetrafluoroborate. In the corresponding vinamidines no mesophase was observed, unless an additional strongly polar group such as a nitro group was present.



A hexagonal columnar mesophase was also observed for hexacatenar vinamidinium salts (127; X = Cl, Br, CF_3SO_3).²⁵³ Polycatenar mesogens have an elongated rigid molecular core bearing one or twohalf-disc-shaped moieties that are formed by terminal alkvl chains.^{254,255} These molecules combine both rodlike and disclike structural features. Hexacatenar mesogens have six terminal alkyl chains, and they typically form columnar mesophases. The hexacatenar vinamidinium salts have a melting point that is only slightly above room temperature and have a mesophase stability range of 100 or more degrees centigrade. The mesophase stability range depends on the counterion, with higher mesophase stability for the chloride and bromide salts than for the triflate salt. The corresponding perchlorate salt does not exhibit a mesophase. The authors rationalized this by arguing that small polarizable anions tend to stabilize the mesophase, whereas bulky hard anions destabilize the mesophase. The extended core length in the hexacatenar vinamidinium salts seems to be beneficial for the stability of the mesophase. So far,



no lamellar mesophases have been obtained for the vinamidinium salts.

4. Metal Carboxylates

4.1. Alkali Metal Alkanoates

Alkali metal alkanoates are called "soaps", and they are well-known types of anionic surfactants. Their general formula is $C_nH_{2n+1}COO^-M^+$, where M = Li, Na, K, Rb, Cs. The alkali metal soaps are soluble in water, wherein they form micelles and lyotropic mesophases at high soap concentrations. The thermotropic mesomorphism of alkali metal alkanoates was first described in 1910 by Daniel Vorländer, who noticed the double-melting behavior of these compounds.²⁵⁶ Later work by other authors showed that the alkali metal alkanoates display a rich polymorphism with several phase transitions between the crystalline state and the isotropic liquid. However, a wide spread of the reported phase transition temperatures is noticed, and this can partially be explained by the fact that some of the phase transitions are difficult to determine visually or by polarizing optical microscopy.

Vold and Vold were able to observe six different phases for anhydrous sodium palmitate (sodium hexadecanoate) by a combination of microscopy and dilatometry.²⁵⁷ These authors introduced a nomenclature for the description of phases, which is still in use today. In order of increasing temperature, these phases are curd fiber phase, subwaxy phase, waxy phase, subneat phase, neat phase, and isotropic liquid. The curd fiber phase is the phase that is stable at room temperature. It is a crystalline phase, consisting of microfibrous aggregates. The subwaxy phase cannot be distinguished from the waxy phase by visual inspection, but the transition from the subwaxy to the waxy phase can be detected by dilatometry. These phases have a higher transparency than the curd fiber phase, and individual fibers or micro crystals are no longer detected. The subneat phase is more plastic than the waxy phase, and the texture observed by polarizing optical microscopy is grainier. The transition from subneat to neat phase can be detected by polarizing optical microscopy by the appearance of the focal conic texture (typical for the smectic A phase). At the transition, there is also a loss of mechanical rigidity of the phase and the neat phase has a turbid (cloudy) appearance due to strong light scattering. The transition from the neat phase to the isotropic liquid is easily detected by polarizing optical microscopy because of the disappearance of birefringence. In bulk samples, this transition is characterized by the development of a meniscus and by the free movement of air bubbles through the molten phase. Upon cooling, no supercooling is observed for the formation of a phase from the higher temperature phase, except for the formation of the curd fiber phase from the subwaxy soap. The authors correctly interpreted the transition as successive stages of the melting process and considered the phases between the crystalline phase and the isotropic liquid as liquid-crystalline phases. The neat phase was compared with the smectic A phase, while

it was assumed that the other mesophases are highly ordered smectic phases. In a subsequent paper, the authors studied the phase transitions for different sodium alkanoates with an even number of carbon atoms.²⁵⁸ They distinguished an additional phase, the superwaxy phase, between the waxy and the subneat phase. It is the superwaxy-to-subneat transition that is the easiest to identify of all the phase transitions because a marked volume change occurs, and the transition is accompanied by a pronounced increase in translucence and by a decrease in rigidity. The superwaxy-to-subneat phase transition was previously considered as the transition from the crystalline state to the mesophase.²⁵⁶ The sodium alkanoates can be divided into three groups, depending on the chain length. For the compounds with intermediate chain length (12-20 carbon atoms), the subneat phase changes to the neat phase, and the neat phase melts to the isotropic liquid. For the compounds with long alkyl chain (22 and more carbon atoms), the subneat phase is transformed into the isotropic liquid in a single step, without going through the neat phase. The compounds with shorter alkyl chains (6-10)carbon atoms) do not show a subneat phase. Binary mixtures of different anhydrous sodium alkanoates have been investigated,²⁵⁹ and the enthalpy changes at the phase transitions of the sodium soaps were determined.²⁶⁰

The work of Vold and co-workers enabled the description of the visual appearance of the different phases of sodium alkanoates, as well as the volume changes of the compounds as a function of the temperature, but the authors could not explain the structural changes associated with the phase transitions at a molecular level. The earliest X-ray diffraction studies were made on sodium soaps in the solid state.^{261,262} Nordsieck et al. have studied the different phases of sodium palmitate, C₁₅H₃₁COONa, by hightemperature X-ray diffraction.²⁶³ They observed sharp lines in the small-angle region and one or two diffuse bands in the wide-angle region. They concluded from the diffraction bands in the wide-angle region that the molecules are packed in a hexagonal lattice and that they can rotate freely around their long axis. However, no structural data were derived from the sharp diffraction peaks in the small-angle region. Chapman has shown by infrared spectroscopy that the alkyl chains are disordered and that their conformation is similar to that of liquid paraffin in all the high-temperature phases from the subwaxy phase to the isotropic liquid.²⁶⁴ The subneat phase is the only phase of a sodium soap that is miscible with the corresponding fatty acid.²⁶⁵

Skoulios and Luzzatti studied the different phases of anhydrous sodium alkanoates by X-ray diffraction and proposed structural models.^{266,267} Two characteristic structural types were distinguished: a ribbon structure (Figures 10 and 11) and a sheet structure (Figure 12). The fundamental difference between the two structures can be traced to the physical state of the polar groups. The polar groups are in the molten state in the sheet structure, whereas they are in the crystalline state in the ribbon structures. Because the polar groups can adopt different polymorphic forms



Figure 10. Arrangement of the polar groups of alkali metal alkanoates in ribbons. Reprinted with permission from *Acta Crystallographica* (http://journals.iucr.org), ref 267. Copyright 1961 International Union of Crystallography.



Figure 11. Ribbon structure of alkali metal alkanoates. Reprinted with permission from *Acta Crystallographica* (http://journals.iucr.org), ref 267. Copyright 1961 International Union of Crystallography.



Figure 12. Model for a sheet structure of alkali metal alkanoates. Reprinted with permission from *Acta Crystallographica* (http://journals.iucr.org), ref 267. Copyright 1961 International Union of Crystallography.

in the crystalline state different types of ribbon structures occur. The subwaxy, waxy, superwaxy, and subneat phases have all a ribbon structure. The structure consists of a set of parallel ribbons, indefinite in length and packed in a rectangular array. The polar carboxylate groups are localized as a double layer in a polar region of finite width and infinite length and the polar groups thus form the ribbons. These ribbons occupy the lattice points of a twodimensional centered rectangular lattice (2D symmetry group *cmm*). The alkyl chains are totally disordered (i.e., they are in a liquid state), and they fill the space between the ribbons. The ribbons take in crystallographic positions in one plane, but there is no coherence in their length direction: they can glide with respect to each other, parallel to their elongation direction. The structure of the subwaxy, waxy, superwaxy, and subneat phases differs in the value of the lattice parameters a and b, and in the ribbon length L. For a given phase, the length of the ribbons is the same for all sodium soaps, but the length decreases when the soap is transformed from the subwaxy phase to the subsequent phases at higher temperatures. At increasing temperatures, one notices that the orthorhombic unit cells become more symmetric and tend to form a hexagonal lattice. The area available for a carboxylate group in the cross section of a ribbon (lateral packing area per polar head S) is the same for all phases and for all sodium soaps (~ 24 Å²), and this value is close to the value found in the crystalline phase ($\sim 22.9 \text{ Å}^2$). This indicates that the polar groups are packed in the ribbon in a way similar to the packing in crystals. The neat phase has a lamellar structure (sheet structure), with parallel and equidistant layers. This can be derived from the reciprocal Bragg spacings in the ratio 1:2:3:4. The polar groups are localized in a double layer of infinite extension, separated by the alkyl chains in the molten state. The layers can glide over each other. The neat phase is the only phase for which a strongly dependence of the structural parameters as a function of the temperature is observed: the interlayer spacing decreases with increasing temperature. The surface available for each carboxylate group in the ionic layer ($\sim 40 \text{ Å}^2$) is much larger than in the other phases. This indicates that the polar groups are disordered in the ionic layer.

At room temperature, the sodium soaps exhibit a lamellar crystalline structure. The polar groups and the alkyl chains are regularly packed, and the alkyl chains are in the all-trans conformation. When the compound is heated, the organization of the alkyl chains is lost, and they adopt a disordered conformation. The resulting tensions that result make the lamellar structure to break into ribbons. The length of these ribbons is determined by the equilibrium between the thermal agitation of the alkyl chains and the cohesion of the polar groups. The higher the temperature, the shorter are the ribbons because the thermal agitation of the alkyl chains increases at higher temperatures. At the transition of a superwaxy to a subneat phase reorientation of the ribbons with respect to the long axis of the crystalline lattice is observed, i.e., the rectangular cross section of the ribbons is turned over 90°. The transition of a subneat to a neat phase corresponds thus to a disrupture of the organization of the carboxylate groups. When the polar groups are separated over this distance, the alkyl chains can adopt a disordered conformation over their whole length. This is not the case in the ribbon structures, where total disorder can only occur at the extreme end of the alkyl chains.



Figure 13. Disc structure of alkali metal alkanoates. Reprinted with permission from *Acta Crystallographica* (http://journals.iucr.org), ref 267. Copyright 1961 International Union of Crystallography.

Because of the tight packing of the carboxylate groups in the ribbons, the part of the alkyl chain close to the carboxylate group is forced into an ordered conformation. The chain conformation becomes more disordered at longer distances from the carboxylate group. Not all structure is lost in the isotropic liquid, in the sense that small mesomorphic domains still exist in the isotropic liquid at temperatures well higher than clearing point. X-ray diffraction shows that the structure of the isotropic liquid is rather similar to that of the neat phase.

An additional phase was observed between the superwaxy and the subneat phase for sodium laurate (sodium dodecanoate, $C_{11}H_{23}COONa$).^{266,267} This phase has a body-centered orthorhombic lattice (space group *Immm*) and its structural unit is a flat disc (Figure 13). The polar groups are localized as a double layer in flat discs and the discs pile up in the crystalline lattice. The molten alkyl chains fill up the rest of the unit cell.

Skoulios systematically investigated the alkali metal soaps, namely, the lithium soaps,^{268,269} the sodium soaps,^{266,267,270} the potassium soaps,^{269,271} the rubidium soaps,²⁷² and the cesium soaps.²⁷³ The melting process of the alkali metal soap takes place in two major steps: the first corresponds to the melting of the alkyl chains and the second corresponds to the melting of the polar groups. In general, the melting point of the alkyl chains decreases with increasing alkyl chain length. This can be understood by the fact that for the compounds with the short chain lengths the cohesion forces in the compact organization of the polar groups work against the chain melting process. In contrast, the temperature at which the neat phase appears is virtually independent of the chain length because the appearance of this phase corresponds to a melting of the polar groups. For the lithium soaps, only ribbon structures are observed and no disc structures. For the sodium soaps, a disc structure is observed only for sodium dodecanoate ($C_{11}H_{23}COONa$). For the potassium soaps, only potassium tetradecanoate (C13H27COOK) shows a disc structure. For rubidium soaps, disc structures are observed for the compounds with 16, 18, and 20 carbon atoms. Rubidium behenate (C₂₁H₄₃COORb) exhibits a ribbon structure. On the other hand, no ribbon structures are observed for the cesium soaps, only disc structures. It is interesting to note that the alkali metal soaps do show either ribbon structures or disc structures but never both for the same soap. The only exception is sodium dodecanoate, which has four phases with a ribbon and one phase with a disc structure. The ribbons are arranged according to a centered rectangular lattice in the case of lithium and sodium soaps but according to an oblique lattice for the potassium soaps. Rubidium behenate shows four ribbon structures with an oblique lattice and at higher temperatures two ribbon phases with a rectangular lattice. For the disc structures, the discs are arranged into a centered orthorhombic lattice for the sodium soaps and into an orthorhombic lattice with a centered B-face for the potassium and rubidium soaps. In the case of the cesium soaps, the discs are localized in parallel and equidistant planes. The lateral correlation between the discs is not well defined. The neat phase occurs for the sodium, potassium, rubidium, and cesium alkanoates but not for the lithium soaps. In the neat phase, the area occupied by a polar group increases with increasing temperature. When only the polar groups are crystallized, the nature of the cation plays an important role in the structural organization because its coordination geometry determines the organization of the polar groups and this determines the average orientation of the disordered alkyl chains and the symmetry of the whole of structural elements. When the alkyl chains are in the crystalline state, the role of the polar groups is less pronounced because they have to adapt themselves to the periodic arrangement of the alkyl chains. When both the alkyl chains and the polar groups are in a molten state, the stability of the phase depends on the alkyl chain length and on the nature of the polar groups. The nature of the cation also determines the number of phases that is observed. For instance, three transitions occur in lithium stearate (C₁₇H₃₅COOLi), but seven transitions occur in potassium stearate $(C_{17}H_{35}COOK).^{269}$

The alkali metal discaps of α, ω -dicarboxylic acids were investigated. These compounds contain two polar groups, one at each end of the alkyl chain. The thermal behavior of these disoaps is much more simple than that of the corresponding monosoaps.²⁷⁴ Two types of structures are found. The first type is a lamellar crystalline state in which both the alkyl chains and the polar groups are in a crystalline state. The second type is also lamellar, but with both the alkyl and the polar groups in the molten state. No intermediate structures (discs or ribbons) with the alkyl chains in the molten state and the polar groups in the crystalline state are formed. This can be explained by the fact that the alkyl chains can melt only if the polar groups melt at the same time. The alkyl chains need a free end to form ribbon or disc structures. The melting point of the disoaps is higher than that of the corresponding monosoaps.

The work of Skoulios was restricted to the alkali metal soaps with an even number of carbon atoms. The compounds with an odd number of carbon atoms have been investigated in much less detail. An Italian groups of researchers investigated lithium,²⁷⁵ sodium.²⁷⁵ potassium,²⁷⁶ rubidium,²⁷⁷ and cesium²⁷⁸ soaps with an odd number of carbon atoms by DSC. There is in the literature some dispute about the phase behavior of the lithium alkanoates. For instance, Vold et al.²⁷⁹ could not detect the waxy phase described by Gallot and Skoulios,^{268,269} but observed a viscous, doubly refracting fluid mesophase with hexagonally closed packed chains. Busico et al. reinvestigated the liquid-crystalline behavior of lithium hexadecanoate, C₁₅H₃₁COOLi, and they reported the existence of a neat phase for this compound.²⁸⁰ The thermal behavior of the whole series of lithium alkanoates from lithium formate (1 carbon atom. HCOOLi) to lithium eicosanoate (20 carbon atoms, C₁₉H₃₉COOLi) has been studied by Ferloni and Westrum.²⁸¹ The dynamic disorder of the alkyl chains in the mesophases of anhydrous soaps has been investigated by ¹H NMR.^{282–285} For each successive phase encountered with increasing temperature an increased level of chain motion was observed. The methyl end of the alkyl chain rotates even below room temperature. Ishioka and co-workers investigated the phase transitions of potassium soaps by infrared and Raman spectroscopy.²⁸⁶⁻²⁹⁰ A compilation of the thermal and transport data of the alkali metal alkanoates is available.²⁹¹

The alkali metal salts of fatty acids are well-known examples of ionic liquid crystals, but it is less wellknown that also the alkali metal salts of short chain alkanoic acids (with less than seven carbon atoms) can form mesophases. The mesomorphism was recognized by Vorländer,²⁵⁶ but this type of compound became popular by the work of Ubbelohde and coworkers.^{292,293} The research on mesomorphic alkali metal soaps of short-chain alkanoic acids has been reviewed by Mirnaya et al.²⁹⁴ On the basis of the classic theories for structure-property relationships in liquid crystals, these compounds are not expected to exhibit mesophases. They are lacking the structural anisotropy, which is thought to be a necessary condition for mesophase formation. The length-towidth ratio of the carboxylate anion in the shortchain alkanoates does not exceed two, whereas in classic liquid crystals this ratio often exceeds five. The presence of a mesophase in the short-chain alkanoates is probably due to the anisotropy in the distribution of the electric charges of the ions rather than to the geometrical anisotropy.²⁹⁴ Ubbelohde investigated in particular the mesophases of sodium *n*-butyrate and sodium isovalerate.²⁹⁵⁻³⁰⁰ The shortchain sodium alkanoates do not display the large number of mesophases observed for the long-chain sodium alkanoates: only one or two mesophases were found. The transition temperatures for the crystalline-to-mesophase transition are in the short-chain alkanoates ca. 100 °C higher than in the long-chain alkanoates. Sodium isovalerate has one solid phase, forms a mesophase at 188 °C, and clears at 280 °C. Sodium *n*-butyrate has three solid phases, forms a mesophase at 252 °C, and clears at 324 °C. The mesophases were identified as smectic A or neat phases by polarizing optical microscopy.³⁰¹ Large differences were observed for the domain sizes in the smectic melts. The domain sizes of sodium isovalerate $(500 \ \mu m)$ are about 25 times larger than those of sodium *n*-butyrate (25 μ m).³⁰¹ The domain size is independent of the temperature. A larger domain size points to a higher mesophase stability. The dynamic properties of the short-chain sodium carboxylates have been studied by NMR spectroscopy (1H, 2H, and ²³Na nuclei).^{302–307} Sodium-23 NMR spectroscopy is a very sensitive technique for the detection of phase transitions because the shape of the sodium-23 free induction decay (FID) changes drastically when the sample undergoes a transition. Also the spin-lattice relaxation time can be used for the detection of phase transitions. Fast diffusion of the carboxylate groups was observed by spin-echo diffusion measurements and by the frequency dispersion of the proton spinlattice relaxation time. Anion diffusion coefficients D of the order of 10^{-6} cm² s⁻¹ have been found in both the mesophase and the isotropic melt of sodium isovalerate and sodium *n*-butyrate. The cation also has an influence on the mesophase stability of the short-chain alkanoates, in the sense that the shortest chain for which a mesophase is formed depends on the cation. No mesophase is formed by the shortchain lithium alkanoates. The smallest mesogenic salts for the other alkali metal salts are sodium butyrate, potassium butyrate, rubidium pentanoate, and cesium hexanoate.³⁰⁸ Although sodium isovalerate forms a mesophase, not all sodium salts of branched short-chain alkanoic acids do. For instance, sodium 2-methylbutyrate and sodium isobutyrate are non-mesomorphic.²⁵⁶ Plesko et al.³⁰⁷ proposed as an ionic bilayer structure as the model for the mesophase of the short-chain alkanoates and compared this model with that of a sandwich structure proposed by Ubbelohde and co-workers²⁹³ (Figure 14). The sodium ions and the carboxylate groups are arranged in a double layer, each half of which is electrically neutral. Each sodium ion is surrounded by carboxylate groups and vice versa. The bilayer can be imagined as being formed by ion pairs of sodium ions and carboxylate ions with interdigitated polar groups. This arrangement is more stable than a sandwich structure, in which the carboxylate groups would be situated above and below a layer containing sodium ions. In such a sandwich structure, there would be strong electrostatic repulsion between the sodium ions within the ionic layer and the carboxylate groups above and below the sodium ion layer. X-ray diffraction studies on the short-chain sodium alkanoates have shown that the structure of the mesophase resembles that of the crystalline solid phase.³⁰⁹ In fact, there is much less difference between the structure of the mesophase and the solid phase in the case of the short-chain sodium alkanoates than in the case of the long-chain sodium alkanoates. The interlayer spacing does not change much as a function of the temperature. The enthalpy and entropy changes associated with the phase transitions of the short-chain alkali metal alkanoates have been studied by Ferloni et al.³¹⁰

Mirnaya and co-workers have investigated the binary phase diagrams of alkali metal alkanoate systems, in an attempt to increase the mesophase



Figure 14. Schematic drawing of the possible arrangement of the alkanoate groups and sodium ions in short-chain sodium alkanoates. (a) Sandwich structure; (b) ionic double layer. Adapted from ref 307.

range by lowering the melting point and increasing the clearing point.^{294,308} Three different types of phase diagrams can be distinguished. First, in a system of two mesomorphic components, a continuous mesophase is observed in the phase diagram. An example of such a binary system is sodium n-butyrate + potassium n-butyrate.³¹¹ Second, in a system of one or two mesomorphic components, one or two limited mesophase ranges can exist. An example is the system sodium n-butyrate + rubidium n-butyrate.³¹² Third, in a system containing two non-mesomorphic components, one or two mesophases can be formed. This is a very interesting case because a mesophase is induced by a mixing of two non-mesomorphic compounds. Examples are the systems sodium acetate + potassium acetate, ³¹³ sodium propionate + potassium propionate, ^{314,315} and sodium *iso*-butyrate + cesium *iso*-butyrate.³¹⁶ The phase diagrams of binary systems of alkali metal alkanoates have been compiled.317

4.2. Alkali Metal Salts of Aromatic Carboxylic Acids

Most scientists working in the field of liquid crystals have the impression that the presence of a long alkyl chain is a condition to have mesomorphic properties. The short-chain alkali metal alkanoates

discussed above show that also compounds with a short chain can exhibit a mesophase. However, in these compounds an alkyl chain is still present, albeit a short one. An intriguing class of compounds are the alkali metal salts of aromatic carboxylic acids because these compounds are liquid crystals without flexible alkyl chains. The liquid-crystalline behavior of these compounds was discovered by Daniel Vorländer in 1910.²⁵⁶ Vorländer investigated the lithium, sodium, potassium, and rubidium salts of benzoic acid. In addition, he investigated the alkali salts of the ortho-, meta- and para-isomers of chlorobenzoic acid, bromobenzoic acid, iodobenzoic acid, methylbenzoic acid, and nitrobenzoic acids. For all these compounds sodium and potassium salts, and a few lithium, rubidium, and cesium salts, have been prepared. Vorländer mentioned only the presence and absence of a mesophase but gave no mesophase identification. These mesophases have often a low viscosity. Demus and co-workers reexamined some of the compounds described by Vörlander: lithium, sodium, potassium, rubidium, and cesium salts of 3-bromobenzoic acid, and the potassium salt of 3-iodobenzoic acid.³¹⁸ Partly they used the original samples prepared by Vorländer 60 years before, and they found no signs of deterioration. By polarizing optical microscopy, these authors determined the transition temperatures and identified the mesophase as a neat phase (smectic A phase). In addition, binary phase diagrams have been constructed by mixing the compounds with other aliphatic and aromatic carboxylate salts. Recently, Binnemans and co-workers screened many alkali metal salts of substituted benzoic acids.³¹⁹ The position of the substituent is of prime importance because only the salts of meta-substituted benzoic acids exhibit mesomorphism. No liquid-crystalline behavior was observed for ortho- and para-substituted compounds. The mesomorphism does not only depend on the type of substituent and its position but also on the type of the alkali metal. The most stable mesophases were observed for the sodium salts. The only mesomorphic salt of unsubstituted benzoic acid is sodium benzoate.

4.3. Thallium(I) and Silver(I) Alkanoates

The behavior of thallium(I) and of silver(I) alkanoates shows some similarity with that of the alkali metal soaps. The mesomorphism of the thallium(I) alkanoates is less complicated than that of the alkali metal alkanoates. The thallium(I) compounds exhibit a lamellar mesophase (neat phase), with an interlayer distance that is between one and two times the length of the molecules in the all-trans conformation.³²⁰ Thallium(I) acetate, propionate, and butyrate salts are not liquid-crystalline, but all the other investigated homologues (up to thallium(I) behenate, C₂₁H₂₃COOTl) are.^{320,321} The effect of chain branching on the thermal behavior has been investigated.³²² The thallium(I) salts of carboxylic acids with α -branching are not mesomorphic, whereas the salts of carboxylic acids with a branch in the β -position exhibit a smectic mesophase. Cheda, Westrum and co-workers determined the heat capacity and the thermodynamic functions of thallium(I) alkanoates by adiabatic calorimetry and by differential scanning

calorimetry.³²³⁻³³⁰ The stability of the neat phase of the thallium(I) alkanoates shows only a limited pressure dependence (up to the experimental limit of 250 MPa).³³¹

Peltzl and Sackmann measured the birefringence (optical anisotropy) and the dispersion (wavelength dependence of the refractive index) of the neat phase of anhydrous thallium(I) alkanoates as a function of the temperature.³³² They made the interesting observation that the optical sign of this uniaxial phase depends on the alkyl chain length. The lower homologues have negative birefringence $(n_0 > n_e)$, whereas the higher homologues have positive birefringence $(n_{\rm e} > n_{\rm o})$. For the homologues with an intermediate chain length a sign inversion of the birefringence was observed at a certain temperature that depends on the alkyl chain length. The positive birefringence of the higher homologues increases with increasing chain length and with decreasing temperature. Revannasiddaiah and Krishnamurti attributed the temperature variation of the birefringence to the internal rotation about the C–C bonds of the alkyl chain.³³³

The binary mixtures of the thallium(I) alkanoates with the corresponding alkanoic acids have been investigated. In these systems, the alkanoic acids act as solvents, and the mesophases in the binary diagram can thus be considered as lyotropic mesophases.^{334–336}

Silver(I) salts of the long-chain alkanoic acids are being used as the silver source in thermographic and photothermographic materials.^{337–340} A visible image is created by reduction of the silver(I) ions to silver(0) nanoparticles during the development process. In contrast to the silver halides, the silver alkanoates in dry imaging materials are quite light insensitive, and this insensitivity toward light increases with increasing alkyl chain length. The most often used silver alkanoates in thermographic materials are silver behenate (C₂₁H₄₃COOAg), silver stearate (C₁₇H₃₅-COOAg), or a mixture thereof. Because of its welldefined layer periodicity with large interlayer spacings, silver behenate also finds application as a lowangle calibration standard for X-ray diffractometers³⁴¹ and for small-angle neutron scattering (SANS) instruments.342

Although the layerlike structure of silver behenate and the other long-chain silver alkanoates has been observed for the first time more than half a century ago,^{343,344} until recently hardly anything was known about the location of the silver ions in the unit cell and about their coordination. This lack of data was mainly due to the difficulties to obtain single crystals of a quality sufficient for single-crystal X-ray diffraction. Tolochko et al. refined the structure of silver stearate by using EXAFS data and unit cell parameters obtained from XRD powder data.³⁴⁵ They found that in the solid state, silver stearate is a dimer, consisting of two silver ions bridged by two bidentate carboxylate groups of the stearate molecules. The silver-silver distance $(2.90 \pm 0.03 \text{ Å})$ in the eightmembered chelate rings is very similar to the silversilver distance in metallic silver. The dimers are stacked one next to another, and there are weak silver—oxygen—silver interactions between neighboring molecules, so that a layerlike structure is formed. The layers containing the silver atoms can be considered as sheetlike coordination polymers.

Silver behenate and the other silver alkanoates do not simply melt in one step upon heating, but they undergo a series of phase transitions before they melt with thermal decomposition.^{346–351} Although some of these transitions are crystal-to-crystal transitions, most of them are mesophase transitions. Bokhonov et al. have studied the thermal behavior of silver laurate, myristate, palmitate, and stearate by DSC, polarizing optical microscopy, and in-situ high-temperature small-angle X-ray scattering.³⁵¹ They found that the silver soaps undergo an irreversible phase transition in the 110-120 °C temperature range. The high-temperature phase has a higher symmetry than the crystalline phase at ambient temperatures. It was also shown that mechanical activation of the compounds by ball-milling induces phase transitions. Binnemans and co-workers investigated the phase transitions of the homologous series of silver alkanoates between silver propionate (C_2H_5COOAg) and silver tetracosanoate (C₂₃H₄₇COOAg), and additionally silver hexacosanoate (C₂₅H₅₁COOAg) and silver octacosanoate (C₂₇H₅₅COOAg).³⁵² Their work illustrated the complex thermal behavior of these compounds. The number and the nature of the phase transitions depend on the alkyl chain length. The thermal decomposition of the silver alkanoates with long alkyl chains proceeds in a liquid-crystalline state (mesophase) and leads to the formation of silver nanoparticles.

4.4. Metal Soaps

The physicochemical properties of the alkanoate salts of the divalent, trivalent, or tetravalent metal ions are very much different from the properties of the alkanoates formed of the alkali metal ions or of other monovalent metal ions. For instance, the alkanoates of the metals in higher oxidation states are not soluble in water, and they do not act as anionic surfactants. On the other hand, they are often soluble in nonpolar organic solvents, in which they form inverse micelles. The alkanoates of divalent, trivalent, and tetravalent metal ions are known as "metal soaps", in order to make the difference with the soaps, which are the alkali metal alkanoates. Not all metal soaps can be considered as ionic compounds, and the bonding between the carboxylate groups and the metal ion can contain a considerable covalent contribution (for instance in the case of copper(II) and rhodium(II) soaps). The mesomorphism of the covalent metal soaps will not be discussed here. The thermal properties of metal soaps have been reviewed by Akanni et al.³⁵³ The review of Binnemans and Görller-Walrand on lanthanide-containing liquid crystals and surfactants describes the mesophase behavior of the rare-earth soaps in detail.¹⁴ The mesophase behavior of the transition metal carboxylates are reviewed in the reviews on metallomesogens.8,17,15 Giroud-Godquin gave a personal account of her work in the field of liquid-crystalline metal soaps.³⁵⁴

Spegt and Skoulios investigated the mesomorphism of the magnesium,³⁵⁵ calcium,³⁵⁶ strontium,³⁵⁷

and barium³⁵⁸ soaps by X-ray diffraction. All these compounds, including the barium soaps, have a lamellar crystalline structure at room temperature.³⁵⁹ The magnesium soaps form a mesophase consisting of cylindrical structural units arranged parallel to each other in a two-dimensional hexagonal lattice. The mesophase can be considered as a hexagonal columnar phase. The cylinders are formed by the carboxylate groups and are surrounded by alkyl chains that are in a molten state. The number of molecules per unit length of the cylinder is independent of the length of the alkyl chain and of the temperature. The packing of the polar groups in the cylinders is similar to that of the crystalline state. The stability and the structure of the cylinders are determined by the organization of the magnesium ions and the carboxylate groups. The thermal behavior of the calcium soaps is more complicated than that of the magnesium soaps.³⁵⁶ These compounds show upon heating a sequence of two phases with disc structures followed by a phase with a cylindrical structure. In one of the disc structures, the discs are arranged in an orthorhombic lattice with centered C-faces. In the other disc structure, the organization is less ordered, and the discs are arranged in layers. In this pseudo-lamellar phase the correlation between the discs is lost. The phase with cylinders is a hexagonal columnar phase and is structurally similar to that described for the magnesium soaps. Hydrates of calcium soaps are dehydrated at the melting point, where these compounds undergo a transition to the mesophase.³⁶⁰ This was illustrated in detail for calcium undecanoate.³⁶¹ The strontium soaps have a lamellar crystalline phase at room temperature, which is transformed upon heating into a mesophase consisting of discs in a monoclinic lattice.³⁵⁷ Further heating results in a cubic mesophase with a body centered cubic lattice. At even higher temperatures, the hexagonal columnar phase was obtained (cylinder structure). In the cubic phase, the polar groups are present on rods of finite length that belong to two interwoven infinite three-dimensional networks.³⁶² The alkyl chains are in the molten state and fill in a continuous manner the space between the interwoven rod network. A cubic mesophase was observed also for calcium *p*-ethylphenyl- ω -undecanoate at room temperature.³⁵⁶ The behavior of the barium soaps is similar to that of the strontium soaps.³⁵⁸ Mirnaya and co-workers investigated the thermal behavior of magnesium soaps³⁶³ and barium soaps.³⁶⁴

Differences are observed in the thermal behavior of zinc(II) and cadmium(II) alkanoates. Whereas the cadmium(II) soaps exhibit liquid–crystalline behavior, the zinc(II) soaps show only solid-state polymorphism and no mesomorphism.³⁶⁵ A monotropic smectic A phase was reported for cadmium(II) decanoate, $(C_9H_{19}COO)_2Cd.^{366}$ The thermal behavior of the longchain cadmium alkanoates is similar to that of the magnesium soaps: a crystalline lamellar phase at room temperature and mesophases consisting of cylindrical structural units that are arranged in a two-dimensional hexagonal lattice.³⁶⁷ The mercury(II) alkanoates are not mesomorphic.³⁶⁸

Quite a lot of attention has been paid to the thermal behavior of the lead(II) alkanoates, and these systems have been studied by different methods that are less common for research on liquid crystals, such as dilatometry, lead-207 NMR spectroscopy, hightemperature Raman and infrared spectroscopy.^{369–371} Also high temperature ¹³C and ¹H NMR studies have been performed.³⁷² Although the mesophase of lead(II) alkanoates have been known for a long time and although it was accepted that lamellar mesophases were formed,^{373,374} there is no agreement on the type of these lamellar phases. For instance, lead(II) decanoate exhibits a crystalline phase, an intermediate phase, and a liquid-crystalline phase. Some authors considered this intermediate phase as crystalline,^{375,376} while others consider it an ordered smectic E phase (crystal E),³⁶⁹ or as a conformationally disordered crystal ("condis" crystal).377,378 The high-temperature phase is labeled either as a smectic A phase³⁶⁹ or a smectic C phase.^{376,379} An early observation of a cubic isotropic phase V_2 could not be confirmed by later work.^{369,380} There are indications that the degree of dissociation of the lead(II) carboxylate bond is small in the isotropic phase³⁸¹ and that lead(II) dodecanoate still contains aggregates in the isotropic liquid.^{382,383} A structural model of the crystalline phase of lead(II) decanoate has been proposed on the basis of X-ray powder diffraction data.384 Single crystals of lead(II) octanoate, lead(II) nonanoate, and lead(II) decanoate have been obtained by a sol-gel technique.³⁸⁵ The binary phase diagram lead(II) decanoate/decanoic acid has been investigated by Adeosun and Akanni,³⁸⁶ and binary phase diagrams of this type were further explored by Cheda and co-workers.^{387,388} The influence of the chain length on the thermal behavior of lead(II) alkanoates has been studied by Adeosun and Sime³⁸⁰ and reinvestigated by Bazuin and co-workers.³⁷⁰ The compounds up to lead(II) dodecanoate show a mesophase behavior similar to that of lead(II) decanoate, whereas lead(II) tetradecanoate and higher homologues show only a highly ordered phase but no smectic A phase. Arenas et al. did not consider lead-(II) tetradecanoate and the higher homologues as liquid crystals.³⁷⁷ A lamellar phase was observed for binary mixtures of long-chain lead(II) alkanoates with phospholipids.389

The mesophase behavior of the lanthanide (or rareearth) alkanoates has been reviewed by Binnemans and Görller-Walrand.¹⁴ The thermal behavior of these compounds shows a strong dependence on both the lanthanide ion and the alkyl chain length.^{390–396} Smectic A phases were found for the mesomorphic lanthanide soaps.

5. Phosphates and Phosphonates

The lithium, sodium, potassium, rubidium, and cesium dihexadecyl phosphates, $(C_{16}H_{33}O)_2PO_2^{-}M^+$ (M = Li, Na, K, Rb, Cs), show a lamellar structure in the crystalline state at room temperature and a hexagonal columnar phase at high temperature. The potassium, rubidium, and cesium salts exhibit an additional $Ia\bar{3}d$ body-centered cubic structure in the temperature range between the crystal and the

columnar phase.³⁹⁷ For the potassium salts, the chain length of the dialkyl phosphates was varied between octyl and octadecyl.³⁹⁸ The mesophase stability range of the mesophase decreases with increasing chain length. The thermal behavior of sodium dihexadecyl phosphate and rubidium dihexadecyl phosphate was investigated by dilatometry.³⁹⁹ It is interesting to note that the alkali metal dialkyl phosphates form a hexagonal columnar phase, whereas a rectangular columnar phase is formed by the alkali metal alkanoates. Beryllium and magnesium dihexadecyl phosphate salts are non-mesomorphic, whereas a hexagonal columnar phase is observed for the corresponding calcium, strontium, and barium salts.⁴⁰⁰ X-ray diffraction studies on the beryllium and magnesium salts above the melting point indicate the presence of ill-developed columnar ordering, which extends over only five repeating units (columnar cybotactic groups in an amorphous liquid). Engberts and co-workers observed thermotropic mesomorphism for the sodium, potassium, and tetramethylammonium salts of di-*n*-dodecyl phosphate, but the mesophases have not been identified.⁴⁰¹

The alkylphosphonate salt of monovalent and divalent metal ions form lamellar structures in the solid state.⁴⁰² However, the only alkylphosphonate that has been reported to exhibit mesomorphic properties is sodium octadecylphosphonate. Zinc(II) alkylphosphonates are not liquid-crystalline.

6. Alkali-Metal Ion Complexes of Neutral Ligands

The ability of crown ethers to form complexes with alkali metal ions is well-known.⁴⁰³ He et al. have shown that liquid-crystalline nematogenic crown ethers (**128**, **129**) retain their complex forming capabilities in the mesophase.⁴⁰⁴ A strong depression of the clearing point (and thus destabilization of the nematic phase) was observed when the mesophase was doped with sodium picrate but not when it was doped with potassium picrate or tetramethylammonium picrate. This difference can be attributed to the selective binding of sodium ions in the crown ether ring. The cation binding effects of the mesomorphic crown ether in the mesophase are comparable with that of classic crown ethers dissolved in methanol.⁴⁰⁵



Nematogenic molecules with a terminal crown ether function and/or lateral chains (130–133) are able to dissolve large quantities of sodium triflate or lithium tetrafluoroborate.⁴⁰⁶ The nematic phase stays stable up to a cation/crown ether ratio of 0.5, and at higher salt concentration an ordered smectic phase is formed. A calamitic molecule with a four-ring core and a lateral crown ether (**134**) can dissolve large amounts of lithium tetrafluoroborate and still exhibit a nematic phase. No induction of smectic phases was found.⁴⁰⁷ The ordering of the ions was explored by lithium-7 and boron-11 NMR, and it was noticed that especially the lithium ions are ordered in the nematic phase. Surprisingly, addition of lithium tetrafluoroborate to a mesomorphic compound with a core of three aromatic rings and with a lateral crown ether group destroys the liquid–crystalline phase, even at a low salt concentration.⁴⁰⁸



Percec and co-workers discovered that addition of sodium triflate to a mesogenic crown ether destabilizes the crystalline phase in favor of the hexagonal columnar phase.⁴⁰⁹ Also in a similar mesogenic crown ether with methacrylate-functionalized alkyl groups, a stabilization of the mesophase was noticed upon addition of sodium triflate.⁴¹⁰ It was even possible to

induce a liquid-crystalline phase in a non-mesomorphic crown ether by complex formation with an alkali metal ion.⁴¹¹ For instance, whereas ligand 135 melts directly to an isotropic liquid at 104 °C, its complex with potassium iodide forms a nematic phase at 54 °C and clears at 101 °C. The transition temperatures can be tuned by a proper choice of the metal ion and of the counterion. Because the transition temperatures and the mesophase depend on the concentration of the metal ion dopant, it was suggested to test these materials as metal-ion sensors. Alkali metal ions promote the self-assembly of folded macrocycles to disc-shaped aggregates and self-organization of these discs into columns. The inclusion of the metal ion stabilizes the columnar structure and increases the clearing point of the mesophase. Potassium iodide stabilizes the hexagonal columnar phase of a discotic 18-crown-6 derivative (136; $R = C_5 H_{11}, C_6 H_{13}, C_7 H_{15},$ $C_8H_{17}, C_9H_{19}, C_{10}H_{21}$).⁴¹²



Rod-coil systems consist of a flexible coil and a rigid rod. Lee and Oh have investigated the influence of complex formation with lithium triflate on the mesophase behavior of liquid-crystalline rod-coil polymers with poly(ethyleneoxide) coils (137).⁴¹³ Whereas the uncomplexed molecule exhibits a smectic B phase, the complexes with 0.05-0.1 equiv of lithium triflate exhibit in addition to the smectic B phase a smectic A phase. The complexes with 0.2–0.3 equiv of lithium triflate do not exhibit a smectic mesophase but form instead a cylindrical micellar phase (which is a cubic mesophase). In a triblock coil-rod-coil molecule, addition of a lithium salt induced cubic and columnar phases in ligands that exhibit only a smectic phase in the free uncomplexed form.^{414,415} The induction of supramolecular structures with curved surface from rodlike molecules can be attributed to the increase of the coil volume fraction resulting from the selective solvation of the added salt in the microphasesegregated poly(ethylene oxide) chains. The poly-(ethylene oxide) chain can be replaced by other poly(alkylene oxide) chains such as poly(propylene oxide) chains.416

Ionic Liquid Crystals



7. Ionic Metallomesogens

In this section, the ionic metal-containing liquid crystals are discussed, with exclusion of the *n*-alkylammonium tetrachlorometalate(II) complexes (section 3.1), the *N*-alkylpyridinium tetrachlorometalate(II) complexes (section 3.4), the metal alkanoates (section 4), and the metal dialkyl phosphates (section 5).

7.1. Complexes of Amines

The adducts of *n*-alkylamine with Lewis acids such as zinc chloride,⁴¹⁷ zinc bromide,⁴¹⁸ copper(II) chloride,⁴¹⁹ or copper(II) nitrate⁴²⁰ are closely related to the n-alkylammonium tetrachlorometalate(II) complexes discussed in section 3.1. Evidence for a smectic liquid-crystalline phase was obtained by X-ray diffraction for the adducts of zinc(II) bromide, $[(C_nH_{2n+1}NH_2)_2Z_nBr_2]$.⁴¹⁸ The corresponding adducts of zinc(II) chloride exhibit a mesophase over a narrow temperature range only.⁴¹⁷ The amine adducts of copper(II) chloride, $[Cu(C_nH_{2n+1}NH_2)_4]Cl_2$, have such a low thermal stability that their mesophase behavior could not be investigated into details,419 but the mesomorphism of the copper(II) nitrate adducts, $[Cu(C_nH_{2n+1}NH_2)_4](NO_3)_2$, has been studied by DSC and polarizing optical microscopy.⁴²⁰

Serrano and co-workers observed a smectic A phase for complexes formed between silver(I) nitrate or silver(I) tetrafluoroborate and *n*-alkylamines: $[Ag(C_nH_{2n+1}NH_2)_2](NO_3)$ or $[Ag(C_nH_{2n+1}NH_2)_2](BF_4)$.⁴²¹ On the basis of X-ray diffraction data a bilayer model was proposed, and it was assumed that the silver(I) diamine cations adapt an U-shape. The anion-cation arrangement breaks at the clearing temperature. In the isotropic phase, the compounds are very prone to photochemical decomposition. Both lyotropic and thermotropic mesomorphism were observed for bis-(*N*-alkylethylenediamine)silver(I) nitrate complexes such as $[Ag(C_{12}H_{25}NHCH_2CH_2NH_2)_2](NO_3)$.⁴²² These *N*-alkyl substituted ethylenediamine complexes form a smectic A phase.

Simon and co-workers prepared metal complexes of amphiphilic amine ligands that contain both an octadecyl chain and two long oligoethylene oxide chains.⁴²³ The ligands were named annelides and a copper(II) chloride complex exhibited thermotropic mesomorphism (**138**).⁴²⁴



Metal complex formation is able to induce mesomorphism in non-mesomorphic cyclic amines of the type [9]aneN₃ (139), [14]aneN₄ (140, 141), and [18]aneN₆ (142).^{425,426} This is due to the locking of the flexible macrocyclic polyamines into one rigid conformation by coordination to a 3d transition metal. For instance, the octahedral nickel(II) nitrate complex of a [9]aneN₃ amine exhibits a rectangular columnar phase.⁴²⁵ The 2:1 complex of a [18]aneN₆ with cobalt(II) nitrate showed a highly viscous mesophase that was tentatively assigned as a nematic columnar phase (N_C).⁴²⁶ The mesomorphic metal complexes of polyamine dendrimers are discussed in section 8.3.



7.2. Silver(I) Stilbazole Complexes

Systematic work by Bruce and co-workers showed that the silver(I) complexes of substituted alkoxystilbazoles are a fascinating class of metallomesogens with a remarkably rich mesomorphism (**143**; X = BF_4^- , CF_3SO_3 , $C_{12}H_{25}OSO_3$).⁴²⁷ Alkoxystilbazoles are in fact 4-substituted pyridines, and they form twocoordinate linear complexes with silver(I) salts. By variation of the anion, the alkoxy chain length, the number of alkoxy chains or the substituents on the aromatic rings, different mesophases are formed. Although counterions are present, these silver(I) complexes are only formally ionic. No electric conductivity is measured in the mesophase, which indicates that these compounds form tightly bound ion pairs.⁴²⁸ The silver(I) tetrafluoroborate complexes of 4-alkoxystilbazoles with long alkyl chains show smectic A and smectic C phases at high temperatures (200-300 °C), where the complexes undergo thermal decomposition.^{428,429} The compounds are light-sensitive and hygroscopic. Nevertheless, their mesomorphism is of interest because complex formation alters the mesophase behavior of the stilbazole ligands, which show a smectic B phase and a crystal E phase. Moreover, these compounds are one of the few examples of ionic liquid crystals exhibiting a smectic C phase. Upon exchange of the tetrafluoroborate counterions by triflate or nitrate counterions, similar smectic phases with high transition temperatures were observed.⁴³⁰ On the other hand, a nematic phase was found for the triflate complexes with short alkyl chains.⁴³¹ For the compounds with methoxy, ethoxy, and propoxy chains, the nematic phase is monotropic, whereas it becomes enantiotropic for the complex with butoxy chain. The presence of a nematic phase is remarkable because this phase is not expected for ionic liquid crystals. The nematic phase is stabilized by weak anisotropic dispersion forces, and not by strong, isotropic electrostatic forces. It was suggested that the nematic phase of such ionic compounds could be used to increase the efficiency and selectivity of electrochemical processes. The triflate complexes with long alkyl chains show a crystal G phase below the smectic C phase.^{427,430}



In an attempt to reduce the transition temperatures, Bruce and co-workers replaced the rigid small inorganic counterions by dodecyl sulfate (DOS).430,431 This exchange was successful, and the clearing temperatures was lowered from 250 °C to about 180 °C. The thermal stability of the complexes was also enhanced, so that these compounds could be studied by X-ray diffraction methods. Although the anhydrous complexes with short alkyl chains exhibit a nematic phase, the nematic phase was absent in samples that contained a small amount of residual water. A lamellar (smectic) phase was observed instead.431 The dodecyl sulfate complexes with long alkoxy chains show a cubic phase between the smectic C phase and the smectic A phase. The chain length of the alkyl sulfate is important for stabilization of the cubic phase, as a cubic phase is found for dodecyl sulfate and tetradecyl sulfate anions but not for the octyl sulfate and decyl sulfate anions. The absence of the cubic phase in the alkyl sulfate complexes with a short alkyl chain was attributed

to the fact that in these compounds the alkyl sulfate chain does not extend past the rigid core of the cation.⁴³² These complexes have an extended range for the smectic A phase instead of the cubic phase. A re-entrant nematic phase (N_{re}) is found when the smectic A phase first appears in the phase diagram. In systems with a re-entrant nematic phase, the nematic phase appears at temperatures below the stability range of the smectic A phase and not above as usual. X-ray diffraction studies on a complex with octyl sulfate counterions with a re-entrant nematic phase show that it possessed strong cybotactic smectic C fluctuations.⁴³³ This means that prior to the transition from the re-entrant nematic phase to the smectic C phase below it, smectic C domains were already present in the re-entrant nematic phase. The alkyl chain of the alkyl sulfate is more or less parallel to the bis(stilbazole)silver(I) cation in the alkyl sulfate complexes.432 The stilbazole chain length and not the chain length of the alkyl sulfate drives the formation of the smectic mesophases. For the complexes of silver(I) 1.12-dodecvlene disulfate with 4-alkoxystilbazole ligands, a nematic phase was observed at short chain lengths, and smectic A and smectic C phases at longer chain lengths.⁴³⁴ However, the cubic phase was absent. The alkyldisulfate salts have higher transition temperatures than the alkyl sulfate salts.

Lateral fluorination of the stilbazole ligands affects the mesophase behavior, and the change depends on the position on the fluorine ligand.435 4-Alkoxy-3fluorostilbazoles and 4-alkoxy-2-fluorostilbazoles have been used as ligand. A fluoro substituent in the 3-position stabilized the smectic A phase but destabilized the nematic phase (144). The cubic phase was absent for the complexes with dodecyl counterions and the 3-fluoro substitution, whereas in the complexes with triflate counterions and with long alkoxy chain, the crystal G phase was absent as well. A different behavior was observed for the complexes with a fluoro substituent in the 2-position (145). Here both the nematic phase and the cubic phase were promoted at the expense of the smectic A phase. In one complex the phase sequence isotropic \rightarrow nematic \rightarrow cubic was observed. The advantage of this phase sequence is that the cubic phase can now be obtained by cooling of a nematic phase (low viscosity) rather than by cooling of a smectic A phase (high viscosity). Cooling of the nematic phase in a magnetic field resulted in alignment of the molecules and the formation of a monodomain cubic phase. The space group of the cubic phase could be determined by X-ray diffraction on these monodomains and was found to be $Ia\bar{3}d$ (identified by the absence of hklspots with $2h + l \neq 4n$).⁴³³ An unusual metastable phase with tetragonal symmetry, the S_4 phase, has been found in the vicinity of the cubic phase.^{436,437} Because of the rather unpredictable behavior of the appearance of the S_4 phase upon heating or cooling of the sample, it is suggested that the transitions to the S₄ phase are kinetically rather than thermodynamically driven. The fluoro-substituent in the 2-position has a broadening effect on the molecules,

so that the intermolecular attraction forces are reduced. This leads to lower transition temperatures and to a promotion of the nematic phase. The fluoro substituent in the 3-position leads to polarization effects that increase the intermolecular attraction forces, so that the transition temperatures are increased and the formation of smectic mesophases is enhanced.438 A few studies of the physicochemical properties of the silver(I) stilbazoles have been made. The mean polarizabilities $\bar{\alpha}$ of the bis(4-octyloxystilbazole)silver(I) triflate and the bis(4-dodecyloxystilbazole)silver(I) dodecyl sulfate complexes have been measured.439 Birefringence measurements of bis(4-methoxystilbazole)silver(I) dodecyl sulfate and bis(4-ethoxystilbazole)silver(I) dodecyl sulfate have been made in the nematic phase.⁴⁴⁰



The rich mesomorphism of the silver(I) 4-alkoxystilbazole complexes is absent in the complexes of 4-alkoxy-2-stilbazoles and 4-alkoxy-3-stilbazoles. While the ligands are nonmesomorphic, the complexes show only a smectic A phase.

The silver(I) complexes of poly-alkoxystilbazoles are examples of polycatenar mesogens. For the tetracatenar silver(I) dodecyl sulfate complexes of 3,4dialkoxystilbazoles (146), a hexagonal columnar phase was found at long chain lengths, and cubic phase.441 The symmetry of the cubic phase was determined by freeze-fracture electron microscopy, and the space group was identified as $Ia\bar{3}d.^{442}$ No smectic C phase was observed. The compounds that exhibit a cubic phase have a tendency to form a glassy mesophase.⁴⁴³ However, an isotropic glass is formed and not an anisotropic glass as often is observed by supercooling of mesophases. The transition from the columnar phase to the cubic phase was investigated by X-ray diffraction and dilatometry. Both the alkoxy chain length of the 3,4-dialkoxystilbazole ligand and the alkyl chain length of the alkyl sulfate were varied in a further study.⁴⁴⁴ Only hexagonal columnar phases and cubic phases were observed, and the stability of the mesophase increased with increasing chain lengths. The phase behavior of the different compounds can be explained by considering whether the alkyl chain of the alkyl sulfate extends beyond the aromatic core or not. When the alkyl sulfate chain extends beyond the aromatic core it contributes to the terminal chain volume, and there is a tendency to form a cubic mesophase. The silver(I) triflate complexes of 3,4-dialkoxystilbazoles show a mesophase behavior that is similar to that of the alkyl sulfate complexes, but the hexagonal columnar phase appears for long chain lengths only.



The silver(I) dodecyl sulfate complexes of 3,5dialkoxystilbazoles show only a hexagonal columnar phase and no cubic phase (147).⁴⁴⁵ The same behavior is observed for the hexacatenar mesogens formed by the reaction between silver(I) dodecyl sulfate and 3,4,5-trialkoxystilbazoles (148).⁴⁴⁵ The melting points of the compounds are close to room temperature. Both for the 3,5-dialkoxystilbazole and the 3,4,5trialkoxystilbazole complexes of silver(I) triflate a cubic mesophase was observed at shorter chain lengths.



The silver(I) stilbazoles can be considered as amphotropic complexes because they exhibit both thermotropic and lyotropic mesomorphism. The lyotropic mesomorphism of silver(I) dodecyl sulfate complexes of 3,4-dialkoxystilbazoles in a series of solvents (linear alcohols, linear alkanes, cyclic alkanes, and small polar aprotic solvents) was investigated by Smirnova and Bruce.⁴⁴⁶ Depending on the solvent, different mesophases were observed. Interestingly, lamellar phases were observed in the lyotropic systems formed by a small polar aprotic solvent like DMSO, whereas they were absent in the corresponding thermotropic systems.

Structurally closely related to the silver(I) stilbazole complexes are the silver(I) 4-phenyl-4'-azopyridyl complexes (**149**, **150**).⁴⁴⁷ Depending on the substitution pattern, nematic, smectic, or cholesteric mesophases could be obtained. The cholesteric mesophase was observed for a complex in which a cholesteryl group was attached via a flexible spacer to the phenyl ring in the 4-position (**151**). The cholesteric phase could be supercooled by rapid cooling to 0 °C to a glassy solid that exhibited the characteristic iridescent colors and the Grandjean texture of the cholesteric phase. Azopyridine hexacatenar silver complexes showed a hexagonal columnar phase (**152**).⁴⁴⁸ Upon irradiation with UV-light the azopyridines 152

show photoisomerization. These compounds are examples of photoswitchable metallomesogens.



Serrano and co-workers investigated a series of silver(I) complexes of 4-substituted pyridines, comparable with the 4-alkoxystilbazoles studied by Bruce and co-workers, but where the C=C linking group has been replaced either by N=C (153) or OC(O)(154).⁴⁴⁹ Most of the complexes showed a smectic A phase, but the thermal stability of the complexes was low. The mesogenic properties increased in the order $CFSO_3^- < PF_6^- < BF_4^- < NO_3^-$. The most stable mesophases were observed for the anions with the smallest volume. Gallardo et al. reported on the mesomorphism of silver(I) perchlorate complexes of tetrazole-functionalized pyridines (155).450 These compounds exhibit a smectic A phase. Both hexagonal columnar and rectangular columnar phases were observed for silver(I) complexes of polycatenar bentcore pyridines (156).⁴⁵¹ The rectangular columnar phase had c2mm symmetry. Whereas the ligands melted and cleared below 100 °C, the silver(I) complexes were mesomorphic over an extended temperature range. Similar to what was observed for other



silver(I) stilbazole complexes, the compounds with triflate counterions have higher transition temperatures than the compounds with dodecyl sulfate counterions.



7.3. Lanthanide Complexes

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A typical feature of lanthanide complexes is the large contribution of electrostatic effects to the metalligand bonding. Because the 4f valence orbitals of the trivalent lanthanide ions are well shielded from the environment by the filled 5s and 5p orbitals, the 4forbitals do not participate in the bonding. The metal-ligand bond is largely ionic, and covalent contributions can be neglected. By a suitable choice of the ligand, counterion, and lanthanide ion, mesomorphic lanthanide complexes can be obtained. The mesomorphic behavior of the lanthanide alkanoates has been mentioned in section 4.4. The most thoroughly investigated class of compounds are the salicylaldimine Schiff base complexes.452-459 Liquidcrystalline lanthanide complexes have been reviewed by Binnemans and Görller-Walrand.¹⁴ The reader is referred to this reference work for more information on these compounds. Here I restrict myself to new developments in the field.

Piguet and co-workers investigated 5- and 6-substituted 2,6-bis(benzimidazol-2-yl)pyridines and the corresponding lanthanide complexes [LnL(NO₃)₃].^{460–462} Conformational changes (trans-trans \rightarrow cis-cis) occurred upon complexation to lanthanide ions: the *I*-shaped 5-substituted ligands are transformed into U-shaped lanthanide complexes, whereas the Ushaped 6-substituted ligands give I-shaped lanthanide complexes. The 5-substituted 2,6-bis(benzimidazol-2-yl)pyridines are calamitic liquid crystals and exhibit a rich mesomorphism (SmC, SmA, and/ or N). Although it was initially reported that the lanthanide complexes essentially retain the mesomorphism of the ligands, further studies showed that the lanthanide complexes have a low thermal stability and are not mesomorphic.⁴⁶³ Structurally, the bent 6-substituted ligands have structural similarities to banana liquid crystals. However, no mesomorphism was detected. The corresponding lanthanide complexes have the shape of calamitic liquid crystals, but they decompose around 180-200 °C, without evidence of mesomorphism. The absence of mesomorphism is contributed to the spatial expansion brought by the $Ln(NO_3)_3$ core. Liquid-crystalline lanthanide complexes could be obtained by increasing the number of terminal alkyl chains from two to six (157).^{464,465} Interestingly, the type of mesophase depends on the lanthanide ion. For the europium(III) and the dysprosium(III) complexes, a bicontinuous cubic phase (Cub_v) is formed, whereas the corresponding lutetium(III) complex exhibits a hexagonal columnar mesophase (Col_h). Thus, a minor size difference of the lanthanide ion induces a transition between a cubic and a columnar mesophase. A bicontinuous cubic phase is a highly ordered mesophase with the appearance of a viscous isotropic phase.



Binnemans and co-workers described liquidcrystalline f-d complexes, which were called mixed f-d metallomesogens (158, 159).⁴⁶⁶ Their approach consisted of modifying the structures of previously described non-mesomorphic f-d complexes in such a way that a sufficient structural anisotropy was obtained to favor the formation of a mesophase. Such a modification could be achieved by extending the aromatic parts of the central rigid core on one hand and to attach long alkyl chains to the extremities of the core complex on the other hand. Kahn et al. described adducts of lanthanide(III) nitrates with the Cu(salen) complex.⁴⁶⁷ For the light lanthanides, they obtained heterotrinuclear $[Ln(NO_3)_3 \{Cu(salen)\}_2]$ compounds, whereas for gadolinium(III) and for the heavier lanthanides heterobinuclear [Ln(NO₃)₃{Cu-(*salen*)}] complexes were formed. The first examples of mixed f-d metallomesogens are a trinuclear copper-lanthanum complex and a dinuclear coppergadolinium complex. These complexes form a hexagonal columnar mesophase. To investigate the influence of the d-metal ion, adducts were formed between a mesomorphic Ni(salen) complex with six terminal alkoxy chains and a lanthanide nitrate (Ln = La, Gd).⁴⁶⁸ Different alkoxy chain lengths were used: OC₁₂H₂₅, OC₁₄H₂₉, OC₁₆H₃₃, and OC₁₈H₃₇. Trinuclear nickel-lanthanum and nickel-gadolinium complexes $[Ln(NO_3)_3 \{Ni(salen)\}_2]$ were obtained. The compounds exhibit a hexagonal columnar mesophase with rather low melting points. By replacing in the



synthesis 1,2-ethylenediamine by 1,2-diaminobenzene, a more rigid Schiff ligand could be obtained (160).⁴⁶⁹



Lanthanide complexes of a steroid-substituted benzocrown ether (161) have been synthesized.⁴⁷⁰ The metal-to-ligand ratio of all the metal complexes was 1:1. The ligand 4'-[(cholesteryloxy)carbonyl]-benzo-15-crown-5 is a monotropic liquid crystal, displaying a cholesteric mesophase. The lanthanide complexes with nitrate counterions form a highly viscous mesophase, which decomposes at the clearing point. The complexes have a low thermal stability. The transition temperatures change as a function of the lanthanide ion, in the sense that the mesophase stability range becomes narrower when the size of the lanthanide ion decreases. Bünzli and co-workers observed a mesophase for europium(III) nitrate and terbium(III) nitrate complexes of a 1,7-diaza-18crown ether with mesogenic pendant arms (162).471,472 The mesophase was identified as a hexagonal columnar phase.⁴⁷² The authors were able to detect the crystal-to-mesophase transition in the europium(III) and terbium(III) complex by temperature-dependent luminescence measurements. Both the luminescence intensity and the lifetime show distinct changes at the transition temperatures.



Faul and co-workers obtained room temperature liquid crystals by complexation of the sandwiched europium-containing polyoxometalate $[Eu(SiW_9-Mo_2O_{39})_2]^{13-}$ with a series of cationic surfactants.⁴⁷³



For the quaternary ammonium cations with one long chain a hexagonal (columnar?) phase and possible a cubic phase was observed, whereas for the quaternary ammonium cation with two long chains the corresponding europium(III) complexes shows a lamellar phase. Zhang et al. prepared highly ordered luminescent films by interaction between the polyoxometalate anion $[Eu(W_{10}O_{36})]^{9-}$ and the hexadecyltrimethylammonium cation.⁴⁷⁴ Although the thermal properties of the europium(III) compound was not investigated in detail, the presence of an endothermic transition around 40 °C in the DSC trace could point to a mesophase transition.

7.4. Miscellaneous Metal Complexes

Complex formation with metal ions can induce a mesophase in non-mesomorphic macrocycles. For instance, Neve et al. obtained a liquid crystal after N,N'-bis(dodecyloxybenzoyl)-1,10-diaza-4,7,13,16tetrathiacyclooctadecane (163) was treated with silver(I) triflate or silver(I) hexafluorophosphate.⁴⁷⁵ A glassy mesophase was obtained by cooling the mesophase of these compounds to room temperature. Also copper(I)⁴⁷⁶ and palladium(II)⁴⁷⁷ could induce a mesophase in this type of macrocycles. A rigid structural element was not necessary to obtain a mesophase for these N₂S₄ macrocycles. For instance, a lamellar mesophase was obtained for the silver(I) triflate and silver(I) tosylate complexes of *N*,*N*'-bis(hexadecanoyl)-1,10-diaza-4,7,13,16-tetrathiacyclooctadecane (164).478 The liquid-crystalline behavior of palladium(II) complexes of rodlike macrocyclic $[14]aneS_4$ and $[16]aneS_4$ thioethers was investigated by Schröder and Bruce.^{479,480} Depending on the length of the ligand either a monotropic smectic C phase or a monotropic nematic phase was detected.



Cyclopalladation of a mesomorphic 2-phenylpyridine ligand gave initially a dimeric palladium(II)

complex with two chloro bridges. However, by addition of a ligand that is able to break these chloro bridges, such as 1,10 phenanthroline and 2,2'-bipyridine, a monomeric species with a +1 charge was obtained. The 1,10-phenanthroline complexes as well as the 2,2'-bipyridine complexes with AsF_6^- and SbF_6^- were not mesomorphic. However, the complex with 2,2'-bipyridine ligand and a BF_4^- counterion (165) exhibited an enantiotropic nematic phase.⁴⁸¹ This is one of the few examples of nematogenic ionic liquid crystals. Kim et al. found that the smectic B phase of a rod-coil molecule was stabilized when this ligand was used to form an organoruthenium complex.⁴⁸²



Deschenaux and co-workers found that oxidation of a non-mesomorphic ferrocene derivative with silver *p*-toluenesulfonate gave a ferrocenium derivative (**166**), which showed either a monotropic smectic A phase⁴⁸³ or a monotropic rectangular columnar phase.⁴⁸⁴ These systems can be considered as redoxactive liquid-crystalline switches because the mesophase can be switched on or off by changing the oxidation state of the metal.



The liquid-crystalline properties of ionic gold(I) and silver(I) isocyanide complexes have been studied.⁴⁸⁵ The 4-alkoxyphenyl isocyanide (**167**; X = NO₃, PF₆) and 4-alkoxybiphenyl isocyanide (**168**; X = NO₃, PF₆) derivatives of gold(I) exhibit a smectic A phase, while the corresponding silver(I) complexes (**169**, **170**; X = NO₃, BF₄) show smectic A and smectic C phases. The 3,4,5-trialkoxyphenyl isocyanide complexes of gold(I) (**171**; X = NO₃, PF₆) and silver(I) (**172**; X = NO₃, BF₄) exhibit a hexagonal columnar phase. The free ligands are not mesomorphic.





N-Alkylimidazoles form ionic complexes with copper(II) nitrate (173) and zinc(II) nitrate (174) by coordination to the nitrogen atom of the imidazole ring.486 The zinc(II) complexes form a smectic A phase, whereas the copper(II) complexes form a highly ordered smectic phase (possibly a crystal G or J type). The zinc(II) complexes are one of the rare examples of metallomesogens with a tetrahedral coordination. Lin and co-workers prepared silver(I) complexes of N-alkylimidazoles (175; n = 10, 12, 14,16, 18; X = NO₃, BF₄, PF₆, CF₃SO₃).⁴⁸⁷ The Nalkylimidazole ligands are not mesomorphic, but most of the corresponding silver(I) complexes are. For the nitrate series, the compound with the $C_{10}H_{21}$ chain is not liquid-crystalline, whereas the compounds with C₁₂H₂₅, C₁₄H₂₉, C₁₆H₃₃, and C₁₈H₃₇ chain exhibit a smectic A phase. For the ligand with the $C_{16}H_{33}$ chain, also the $[BF_4]^-$, $[PF_6]^-$, and $[CF_3SO_3]^$ salts were prepared; a smectic A phase was found for the $[BF_4]^-$ and $[PF_6]^-$ salt, whereas the triflate salt was non-mesomorphic. The widest temperature range over which the smectic A phase was stable was observed for the $[BF_4]^-$ salt. The silver(I) complexes of N-alkylbenzimidazoles (176) do not show a mesophase. The absence of mesomorphism is attributed to a larger width-to-length ratio of the benzimidazole core.





A hexagonal columnar phase was found for copper(II), nickel(II), and palladium(II) tetrafluoroborate complexes of macrocyclic [b,f,j,n][1,5,9,13]tetraazacyclohexadecine (**177**; M = Cu, Ni, Pd).⁴⁸⁸ The mesophase was stable over a wide temperature range, and the complexes with a short alkyl chain were even at room temperature mesomorphic. The clearing temperature depended on the metal ion and decreased in the order M = Ni > Pd > Cu.



Nonionic oligo(ethylene oxide) surfactants $C_{12}EO_4$, $C_{12}EO_{10}$, $C_{12}EO_{23}$, $C_{16}EO_{10}$ form liquid-crystalline phases upon complexation with transition metal aqua complexes.^{489,490} Ions that have been studied include $[Ni(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$, $[Zn(H_2O)_6]^{2+}$, $[Cd(H_2O)_4]^{2+}$, $[Mn(H_2O)_4]^{2+}$, and $[Cr(H_2O)_6]^{3+}$. The type of mesophase depends on the anion. Nitrate anions induced hexagonal columnar phases, perchlorate ions induce cubic phases, but no mesophase is induced by transition metal chloride salts. The most stable mesophases are observed for the nitrate systems. The water coordinated to the metal ion is necessary for the formation of the mesophase. When the coordinated water is lost upon heating, the mesophase order disappears, but the mesophase can be formed again after rehydration of the system.

Ziessel and co-workers obtained mesomorphic ionic complexes with tetrahedral coordination by complex formation of copper(I) with ligands derived of pyridine-2-carbaldimine (178) or 2,6-pyridine-2,6-dicarbaldimine (179),491 2,2-bipyridine (180),492 and 2,2',6',2"-terpyridine (181).⁴⁹³ Depending on the ligand structure, columnar mesophases of a different symmetry were obtained (hexagonal, rectangular, and oblique phases), as well as a lamello-columnar phase. Faul and co-workers prepared ionic copper(II)containing metallomesogens by addition of a quaternary ammonium salt to the copper(II) complexes of bathophenantrolinedisulfonic acid (182) and bathocuproinedisulfonic acid (183).⁴⁹⁴ Interestingly, it was found that upon addition of the surfactant to the copper(II) of bathocuproinedisulfonic acid, reduction of copper(II) to copper(I) occurred. This reduction from copper(II) to copper(I) was evident from a color change from green to brick red and was attributed to changes in the electrochemical potential due to the energy gain by an optimized packing of the alkyl chains of the surfactant. The interactions between



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the alkyl chains thus lead to an electronic transition at the metal center. The fact that the reduction process is only observed for the complex of bathocuproinedisulfonic acid and not of bathophenantrolinedisulfonic acid can be explained by the induction of a tetrahedral coordination of the copper center by the two methyl groups in the 2- and 9-position of the phenanthroline ring in bathocuproinedisulfonic acid. It is known that a tetrahedral coordination has a stabilizing effect on the copper(I) oxidation state. Complexes of double-tail ammonium cations show thermotropic mesomorphism (**184**), although the thermal behavior is quite complex. Different types of mesophases, such as a hexagonal columnar phase, a rectangular columnar phase and a lamellar phase have been observed. A smectic B phase was identified for complexes of quaternary ammonium ions with a single long tail, but detailed interpretation of the thermal behavior was found to be difficult.

8. Ionic Polymer Liquid Crystals

Polymer liquid crystals (PLCs), also known as liquid-crystalline polymers, combine the properties of polymers with those of liquid crystals.495-497 Flexible polymers can be transformed into liquid crystals by incorporation of rodlike or disclike mesogenic groups in the basic polymer motif. These mesogenic groups can be part of the backbone (main-chain polymer liquid crystals) or can be attached by a spacer to the backbone (side-chain polymer liquid crystals). Hybrid forms are possible as well.⁴⁹⁸ The main-chain polymer liquid crystals have inherently rigid structural elements in the backbone. Two major groups of main-chain polymer liquid crystals are known. The first group consists of polymers made of stiff rodlike monomers.⁴⁹⁹ In the second group, the mesogenic groups in the backbone are decoupled by alkyl spacers that make the polymer backbone somewhat flexible.⁵⁰⁰ The spacer allows independent movement of the mesogenic groups. Most of the mainchain polymer liquid crystals belong to the second group. The side-chain polymer liquid crystals have three main structural components: the polymer backbone, the spacer, and the mesogenic group. The polymer backbone is the structural unit that gives polymeric properties of the material. The spacer is used to attach the mesogenic groups to the backbone, and the spacer allows independent movement of the mesogenic groups so that they can orient. The alignment of the mesogenic groups causes the liquidcrystalline behavior. Short spacers promote the formation of a nematic phase, whereas long spacers promote the formation of smectic phases.

Ionomers are ion-containing polymers.^{501,502} They contain a small amount of abound ionic functionality, such as carboxylic acid or sulfonic acid groups neutralized with a metal cation, whose aggregation produces dramatic changes in the materials properties. The polymer chains are ionically cross-linked through nondirectional ionic bonds, which are strong but thermally labile. Unlike chemically cross-linked polymers, they melt upon heating and reform upon cooling. In section 8.1, the main-chain ionic polymer liquid crystals are described, whereas section 8.2 is devoted to the side-chain ionic polymer liquid crystals. Ionic liquid crystals based on dendrimers will be discussed separately in section 8.3.

8.1. Main-Chain Ionic Polymer Liquid Crystals

Main-chain polymer liquid crystals often have remarkable mechanical properties and thermal stabilities. However, these materials have poor transverse and compressive strengths in contrast to the very high axial strength. Another problem is their poor miscibility with and adhesion to other polymers, so that it is difficult to produce polymer blends of main-chain liquid-crystalline polymers and conven-

tional polymers. Hara and co-workers developed main-chain ionic polymer liquid crystals by introducing ionic groups and ionic bonds into the polymer chain to obtain better tensile and compressive properties.^{503–505} They have chosen a wholly aromatic polyester based on random copolymerization of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, a 5-sulfoisophthalate salt, and hydroquinone (185). The meta-substituted 5-sulfoisophthalate salt not only introduces ionic groups into the polymer but also results in kinks in the polymer chain. The polymer derived of sodium 5-sulfoisophthalate salt exhibits a nematic phase over a wide temperature range up to temperatures above 380 °C.⁵⁰³ Upon an increase in content of the ionic monomer from 0 to 10 mol %, a decrease of the melting point was observed due to a decrease of the chain rigidity. Above 5 mol % of ionic monomer, a glass transition was observed. The step of the glass transition becomes larger with increasing ionic content. Upon a further increase of the content of the ionic monomer to 15 mol %, the melting peak was no longer observed in the DSC thermogram, but the height of the glass transition step increased further. The Na⁺ ion in the ionic polymers can be replaced by a divalent ion $(Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+})$.⁵⁰⁴ Ionic naphthalene thermotropic liquid crystals with 1 mol % of ionic groups have been prepared. The polymers with calcium ions retain a high molecular weight and exhibit at the same time good mechanical properties and a high thermal stability. The ionic polymer with other divalent ions have lower molecular weights.



Paleos and co-workers investigated the mesomorphic properties of oligomeric viologens (4,4'-bipyridinium salts) (186; n = 4, 10, 12).⁵⁰⁶ Main-chain liquid-crystalline viologen polymers have been intensively studied by Bhowmik (187).507-512 These compounds exhibit both thermotropic and lyotropic mesomorphism. The thermotropic phases were identified as smectic phases. The classic preparation method is the Menshutkin reaction of 4,4'-bipyridine with α, ω -methylene ditosylate in acetonitrile. These polymers have interesting properties such as electric conductivity, electrochromism, photochromism, and thermochromism, besides their mesophase behavior. Another type of viologen polymers was prepared by the reaction between 4,4'-bipyridine with the ditosylate of trans-1,4-cyclohexanedimethanol (188).⁵¹³ Also viologen polymers with ortho-, meta- and paraxylyl units in the backbone, and with bromide, tosylate or triflimide counterions (189-191) are known.⁵¹⁴ Interestingly, these polymers with the meta- and para-xylyl unit and triflimide counterions form a lyotropic mesophase at room temperature in the ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate and triethyloctylammonium triflimide.⁵¹⁵ The polymer concentration at which the lyomesophase is formed is identical to that in methanol but is much lower than that in polar aprotic solvents. No lyotropic mesomorphism was observed for the viologen polymer with the *ortho*-xylyl unit and triflimide counterions.



Poly(pyridinium)salts with tosylate and triflimide counterions (**192**; X = TsO, N(SO₂CF₃)2) exhibit both thermotropic mesomorphism and light-emitting properties.^{516,517} The tosylate salt was prepared by the ring-transmutation polymerization reaction of 4,4'-(1,4-phenylene)bis(2,6-diphenylpyrylium tosylate) with 1,12-diaminododecane in DMSO at 145–150 °C. The triflimide salt was obtained by a metathesis reaction between the polymer with tosylate counterions and lithium triflimide in acetonitrile. The triflimide polymer had a better thermal stability than the tosylate polymer. The photoluminescence of these ionic polymers has been studied both in solution and in the solid state.



An ionic liquid-crystalline aromatic ester was obtained by high-temperature solution polycondensation of terephthaloyl chloride with the quaternary triethyloctylammonium salt of hydroquinonesulfonic acid (**193**).⁹⁰ This work has been extended to ionic polymers with tributyloctylammonium, tributyldodecylammonium, and trimethylhexadecylammonium counterions.⁹¹ A smectic B and at higher temperature a smectic A phase was found for a polymalonate polymer with biphenylene units in the main-chain and with pyridinium salts in the side-chain. $^{\rm 200}$



8.2. Side-Chain Ionic Polymer Liquid Crystals

An approach that is often used to obtain side-chain polymer liquid crystals is to attach a mesogenic group via a spacer to methacrylic acid, followed by polymerization of the methacrylic acid groups. Bazuin and co-workers investigated tail-end amphiphiles of the type $poly(\omega$ -pyridinium alkyl methacrylates) with various 4-substituted pyridinium bromide groups and spacer lengths (194).^{518,519} Also the corresponding polymers with alkylsulfonate counterions have been considered.⁵²⁰ Haramoto and co-workers described high-molecular weight ionic liquid-crystalline polymers with a 4-(1,3-dioxan-2-yl)pyridinium group in the side-chain (195).⁵²¹ An ionic side-chain polymer liquid crystal with sodium counterions could be prepared by partial alkaline hydrolysis of liquidcrystalline polyacrylates bearing either a phenyl benzoate or a cyanobiphenyl group in the sidechain.^{522,523} In the case of the polyacrylate bearing a 4-cyanophenyl benzoate group, the partial hydrolysis by sodium hydroxide gave the sodium salt of benzoic acid (196), whereas in the case of the polyacrylate with the cyanobiphenyl group the hydrolysis reaction resulted in the sodium salt of acrylic acid (197). The polymers exhibit a nematic phase. The presence of the ionic groups depressed the clearing point but had little effect on the glass transition temperature. A study of the orientation of these ionic polymer liquid crystals in the nematic phase shows that the ionic groups make it more difficult to align the polymer in a magnetic field. This is due to the reduction of the chain mobility by the formation of ionic aggregates. The maximum alignment was obtained closed to the clearing point.⁵²³ In side-chain liquid-crystalline polymers bearing a 15-crown-5 unit and that exhibit a smectic A phase and a nematic phase, it was found that upon complex formation with sodium triflate the clearing point increased and at high salt concentration (more than 0.5 equiv of sodium triflate) the smectic A phase was suppressed in favor of the nematic phase (198, 199).⁵²⁴ This is surprising because one expects that the presence of ionic components would stabilize the smectic phases. The ionic liquid crystal poly(*w*-pyridylpyridinium dodecyl methacrylate) bromide can form, without detrimental effects for the mesophase behavior, a hydrogenbonded complex with 4-octylphenol.⁵²⁵ Barmatov and co-workers investigated liquid-crystalline ionomers

containing alkali metal ions, alkali-earth metal ions, transition metal ions, and rare-earth ions to establish the effect of the nature of the metal ion on the mesophase behavior.⁵²⁶⁻⁵³⁶ Parameters that have an influence on the phase behavior are charge and radius of the metal ions, distance between the charged ionogenic group and the polymer backbone, and the molecular mass of the polymer. The metal ions act as points of electrostatic binding of the polymer chains and are capable of forming larger ionic associates (so-called multiplets). However, the formation of ionic links may lead to the growth of structural defects, which suppress the positive influence of charged groups on the clearing temperature. Metal ions induce smectic phases in ionic nematogenic polymer liquid crystals. A chiral nematic phase was detected for a liquid-crystalline ionomer bearing cholesteryl, phenylbenzoate, and carboxylate groups, and with sodium or cobalt(II) ions.537





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Liquid crystals were obtained by quaternization of poly(4-vinylpyridine) with (4-methoxy-4'-biphenylyloxy)alkyl halide mesogenic groups or by spontaneous polymerization of 4-vinylpyridine in the presence of a (4-methoxy-4'-biphenylyloxy)alkyl halide (**200**).^{538,539} These compounds show a smectic A phase above a smectic B or a crystal E phase. Poly(4-vinylpyridinium) salts with cyanobiphenyl or chiral biphenyl mesogenic side groups exhibit smectic A and crystal E phases.⁵⁴⁰ The polymer backbone can also be a

polymethylsiloxane with pyridine groups attached to it via a spacer (**201**).⁵⁴¹ The flexibility of the polysiloxane backbone and the spacer reduces the glass transition temperature and facilitates the smectic organization. Ionic polysiloxanes were prepared by graft polymerization of 4-(4-allyloxybenzyloxy)-4'alkylxybiphenyl) as the mesogenic unit and allyltriethylammonium bromide as the ionic non-mesogenic









unit.⁵⁴² The polymers exhibit both a smectic and a nematic phase.

Linear poly(ethylene imine) polymers can be derivatized to transform them into liquid-crystalline polymers (**202–204**).^{543,544} The poly(ethyleneimine)s can be partially or completely alkylated by an alkyl halide with a pendant mesogenic group. Subsequently, the amine functions can be partially or completely protonated with hydrobromic acid or quaternized with dimethyl sulfate. Because of the two-step process and of the partial reactions, the polymers that are formed can be considered as copolymers. Four different units can be present: the ethyleneimine unit, the alkylated ethyleneimine unit, the quaternized ethyleneimine unit, and the alkylated and quaternized ethyleneimine unit. The compound exhibits a smectic A phase.



Side-chain polymer liquid crystals can be obtained by attaching mesogenic groups covalently via a flexible alkyl spacer to a polymer backbone. It is also possible to attach the mesogenic groups via noncovalent bonds to the polymer backbone by ionic interactions.⁵⁴⁵ In this case, an ammonium-functionalized mesogen forms an ion-pair with sulfonated polymers such as poly(vinylsulfonate) or poly(styrenesulfonate), or with polymers bearing carboxylate groups such as poly(acrylic acid) or poly(methacrylic acid). The first example of an ionically bonded polymer liquid crystal complex was published by Ujiie and Iimura (205).⁵⁴⁶ These authors found a smectic A phase with a partially interdigitated bilayer structure for a polymer with an ion-pair formed between poly(vinylsulfonate) and a quaternary ammonium compound with a pendant nitroazobenzene mesogenic group. Whereas often highly ordered smectic mesophase are observed for quaternary ammonium salts with a pendant mesogenic group, the resulting ionically bonded polymer liquid crystals display a disordered smectic phase (smectic A).^{547,548} It is thus possible to induce disorder in highly ordered mesophases formed by quaternary ammonium salts with pendant mesogenic groups by mixing them with commercially available polymers such as poly(acrylic acid), poly(methacrylic acid), or sodium poly(vinylsulfonate). The effect was more pronounced for the polymers bearing a sulfonate group than for those bearing a carboxylate group. Low molecular weight polystyrenes end-capped by a carboxylate or a sulfonate group were used as the backbone for ionic polymer liquid crystals formed by ionic interaction with quaternary ammonium salts bearing a mesogenic group. 549,550

Long-chain *n*-alkylammonium polyacrylates were synthesized by neutralizing poly(acrylic acid) dis-



solved in ethanol with long-chain primary amines $(206)^{551-553}$ or secondary amines $(207)^{.551}$ The dodecyl, tetradecyl, and didodecyl derivatives show a smectic A phase from room temperature to the temperature where thermal degradation occurs. The hexadecyl, octadecyl, and dioctadecyl derivatives exhibit a smectic B or a crystal E phase at low temperatures and a smectic A phase at high temperatures. The compounds prepared from primary amines have relatively low degradation temperatures (about 90 °C), but those prepared from secondary amines are much more stable (thermal degradation well above 130 °C). Antonietti and co-workers prepared liquid-crystalline polyelectrolyte-surfactant complexes made of poly(styrenesulfonate) and different alkyltrimethylammonium ions.⁵⁵⁴ Also poly(dodecyltrimethylammonium) acrylate has been prepared.555 Tsiourvas et al. investigated poly(vinylsulfonate)s with nalkylammonium, N,N-dimethyl-n-alkylammonium, and N,N-dimethyl-N-cyanopropyl-n-alkylammonium ions.⁵⁵⁶ Interestingly, N,N-dimethyl-N-cyanopropyl*n*-dodecylammonium poly(vinylsulfonate) and *N*,*N*dimethyl-N-cyanopropyl-n-tetradecylammonium poly-(vinylsulfonate) exhibit a body-centered cubic phase (Ia3d symmetry) at low temperatures. The interaction of $poly(\alpha,L-glutamic)$ acid with long-chain primary and secondary amines leads to the formation of side-chain ionic polymer liquid crystals with a smectic B, a smectic C, or a crystal E phase.⁵⁵⁷



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Redox-active ionic liquid-crystalline polymers were prepared by Zentel and co-workers from ferrocenecontaining liquid-crystalline polymers by a redox reaction.⁵⁵⁸ The amount of ionic groups in the polymer can be controlled by the redox reaction. Ionic aggregates acts as cross-linking points. It is thus possible to convert a non-crosslinked polymer in



cross-linked one by a redox reaction, and the process is reversible. Blends of these compounds with partially sulfonated polystyrene combine the properties of the constitutive components.⁵⁵⁹⁻⁵⁶¹

Thünemann and Müllen obtained liquid-crystalline complexes by interaction between polyelectrolytes and large, charged, and conjugated discotic molecules. The polyelectrolyte was either an aminofunctionalized polysiloxane⁵⁶² or a hydrophobic poly-(ethylene imine) (**208**).⁵⁶³ The discotic molecules are already liquid-crystalline themselves, but the polyelectrolyte supported systems show higher order inside the columns and the formation of very large extended columns.



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8.3. Ionic Liquid Crystal Dendrimers

Ionic liquid crystals based on dendrimers have been created by the interaction of carboxylic acids with dendrimers that are functionalized on their periphery with amino groups. An ion-pair is formed by the transfer of the proton of the carboxylic acid to the amino group, resulting in salt-like dendrimer compounds. Commercially available poly(amidoamine)

dendrimers (PAMAM dendrimers) or poly(propylene imine) dendrimers (PPI or DAB dendrimers) of different generations have been investigated. Tsiourvas et al. have described the liquid-crystalline character of salts that were generated by the interaction of poly(propylene imine) dendrimers with 3-cholesteryloxycarbonylpropanoic acid (209).564 These liquidcrystalline dendrimers carrying mesogenic cholesteryl groups exhibit smectic C* phases (chiral smectic C phase) and smectic A phases. An important factor that determines the phase behavior is the degree of protonation of primary amino groups as compared with that of the tertiary ones. Protonation of the tertiary amino groups of the PPI dendrimers is more pronounced for the higher generation dendrimers than for the low generation dendrimers. A mesogenic group is not necessary for the presence of a mesophase in ionic liquid crystal dendrimers. Ujiie et al. obtained ionic liquid crystal dendrimers by interaction between third generation PAMAM dendrimers and alkanoic acids (tetradecanoic, hexadecanoic, and octa decanoic acid). 565 All the three dendrimers showed a smectic A phase. Serrano and co-workers made a comprehensive study of the mesophases formed by the interaction of PAMAM and PPI dendrimers of different generations with decanoic, tetradecanoic, and octadecanoic acid.566 Most of the ionic dendrimers studied showed a smectic A phase, but a columnar phase was observed for the salts of the fifth generation of the PPI dendrimer (containing 64 terminal NH_2 groups). A hexagonal columnar phase was present for the salt formed with octadecanoic acid and a tetragonal columnar phase for the salt formed with tetradecanoic acid. The PPI-decanoate salts are room temperature ionic liquid crystals. The transition temperatures increase with an increase in the chain length of the alkanoate. The salts derived of the PAMAM dendrimers have higher transition temperatures than the corresponding PPI salts due to the presence of hydrogen bonds within the structure of the PAMAM dendrimers. The fact that liquid crystal phases are obtained for these ionic dendrimers, although no aromatic mesogenic groups are present. indicates that ionic interactions play an important role in the stabilization of mesophases.

Tschierske and co-workers prepared ionic liquid crystals with unconventional mesophase structures by interaction of poly(propylene imine) dendrimers with T-shaped amphiphilic carboxylic acids, which contain a *p*-terphenyl core (**210**).⁵⁶⁷ The mesophase structure is governed by different factors such as the temperature, the generation of the dendrimer, the ratio of dendrimer to carboxylic acid, and the length of the lateral polyether chain in the T-shaped carboxylic acids. The mesophases observed include the smectic A phase, two different square columnar phases (*p*4*mm* and *p*4*gm* symmetry), a mesophase combining a layer structure with a hexagonal organization of columns, and two mesophases with an unknown structure.

Complex three-dimensional structures were observed by Percec and co-workers for the alkali metal salts of minidendritic carboxylates (first generation monodendrons), which are in fact the alkali metal



salts of 3,4,5-trialkoxybenzoic acids.⁵⁶⁸ The compounds self-assemble at low temperatures into supramolecular cylinders that self-organize in two-dimensional rectangular columnar (c2mm symmetry) of hexagonal columnar lattices (p6mm symmetry). At high temperatures these compounds self-assemble into three-dimensional cubic lattices of $Pm\bar{3}n$ or $Im\bar{3}m$ symmetry. The rectangular columnar phases are formed by the sodium compounds only. The structure of the cubic mesophase of the rubidium salt of a second-generation monodendron containing a carboxylate group and partially fluorinated alkyl chains was determined (**211**).⁵⁶⁹

Lattermann and co-workers investigated the mesophase behavior of transition metal complexes of branched polyamine complexes.^{570,571} These ligands (**212**, **213**) can be considered as first and second generation dendrimers. Complexes with CoCl₂, NiCl₂, Ni(NO₃)₂, ZnCl₂, CuCl₂, Cu(SCN)₂, and Cu(NO₃)₂



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have been prepared. Two different types of complexes are formed: ionic pentacoordinate complexes $[MX(L)]^+X^-$ and neutral hexacoordinate complexes $[MX_2(L)]$. The dendrimers are tetradentate ligands. The coordination polyhedron of the pentacoordinate complexes can be either a trigonal bipyramid or a square pyramid, whereas the hexacoordinate complex has an octahedron as coordination polyhedron. The nickel(II) complexes have a octahedral coordination, while the cobalt(II) and copper(II) complexes have a trigonal bipyramidal coordination. The coordination of the zinc(II) complexes could not be determined unambiguously. All the complexes of the first generation dendrimer ligand 212 were mesomorphic (hexagonal columnar phase), except the complex of $Ni(NO_3)_2$. The ligand itself is non-mesomorphic. These metallomesogens form a mesophase at moderate temperatures. Some are even at room temperature liquid-crystalline. The complexes either form a glass in the solid state, which sometimes crystallizes out after heating above the glass transition temperature. The second-generation dendrimer 213 is a monotropic liquid crystal (hexagonal columnar phase), and its complex with CuCl₂ shows an enantiotropic hexagonal columnar mesophase. The coordination polyhedron of copper(II) is assumed to be a trigonal bipyramid in this complex. In all these examples, it is evident that complex formation with a metal ion is beneficial for the presence of a mesophase: either mesomorphism is induced in a



non-mesomorphic ligand or a monotropic mesophase is stabilized to an enantiotropic mesophase.



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9. Applications of Ionic Liquid Crystals

9.1. Ion-Conductive Materials

One of the goals of molecular electronics is the development of ion-conductive materials. To be useful at a molecular level, this ion conductivity should be anisotropic, which means that the ion conductivity depends on the direction in which it is measured. Ionic liquid crystals are very promising candidates to design anisotropic ion-conductive materials because they have an anisotropic structural organization and because they contain ions as charge carriers. Moreover, the long alkyl chains of mesogenic molecules can act as an insulating sheet for the ionconductive channel. Depending on the type of mesophase, materials for one-dimensional or two-dimensional ion conduction can be obtained.⁵⁷² Liquid crystals with a columnar mesophase can be used to create a material for one-dimensional ion conduction. In this case, ion conduction takes place in the direction of the column axis. Two-dimensional ion conduction can be observed for smectic liquid crystals, where ion conduction can take place inside the smectic layers. To observe a high anisotropy for the ion-conduction in ionic liquid crystals, it is important to have aligned samples, so that a liquid-crystalline monodomain is obtained. The boundaries between unaligned polydomain are detrimental for ion conduction. If one wants to make materials on the basis of ionic liquid crystals that keep their anisotropic ion conductivity for a long time, it is necessary to stabilize the ordered molecular arrangement of the liquid-crystalline monodomain. This can be done by in-situ photopolymerization of aligned liquid-crystalline molecules with polymerizable groups. Thermal polymerization has to be avoided because the thermal agitation can destroy the mesophase order.

The earliest work on ion-conductive liquid crystals was directed to the design of materials with high ion



Figure 15. Illustration of the anisotropic ion conduction for self-organized ion conductive materials. Reprinted with permission from ref 578. Copyright 2000 American Chemical Society.

conduction, but this work failed to observe high anisotropy for ion conduction because of the difficulties in obtaining well-oriented liquid crystal monodomains. Poly(ethyleneoxide)s have been functionalized by mesogenic groups to obtain new functional ion-transporting materials.⁵⁷³⁻⁵⁸² Hubbard et al. used the magnetic field of a superconducting magnet (field strength 7.1 T) to align an ion-conductive polymer liquid crystal doped with lithium triflate.574 The authors observed that the conductivity in the direction parallel to the smectic layers is five times higher than the conductivity in the direction perpendicular to it. Kato and co-workers prepared liquid-crystalline complexes of lithium triflate and dimeric molecules containing a poly(oxyethylene) chain (Figure 15. 214).⁵⁷⁶⁻⁵⁸² The complex formation with lithium ions resulted in a thermal stabilization of the mesophase. Although these complexes could be aligned on a glass surface with comb-shaped gold electrodes, attempts to obtain aligned monodomain samples on ITO electrodes failed. Not only have Li⁺ ions, but also Na^+ , K^+ , Mg^{2+} , and Sc^{3+} ions (always as triflate salt),⁵⁸² have been used as charge carriers in these materials. For the alkali metal salts, the conductivities increase with the increase in the cation size in the isotropic liquid. The lithium ion shows the highest conductivity of the alkali metal ions in the smectic A and smectic B mesophase. A remarkable sharp increase in the ionic conductivity of the lithiumcontaining system was observed when the material enters the smectic A phase upon cooling from the isotropic liquid. The ionic conductivity of the Mg²⁺ and of the Sc^{3+} ion is much lower than that of the alkali metal ions, both in the mesophase and in the isotropic liquid. Perfluoroalkyl chains have been incorporated in the smectogenic molecules in an attempt to stabilize the smectic layers by the strong intermolecular interaction between the perfluoroalkyl chains and because of the immiscibility of polyoethylene and perfluoroalkyl chains.⁵⁸⁵ Percec and coworkers measured the ion conductivity in a liquidcrystalline crown ether complex.⁴⁰⁹



Imidazolium tetrafluoroborate ionic liquid crystals exhibiting a hexagonal columnar phase where designed by Kato and co-workers.¹⁶⁰ It was possible to obtain a macroscopically homogeneous alignment of the columns by shearing the mesomorphic compounds between two microscope glass slides. No rubbing treatment of the glass slides was necessary to transform the polydomain structure into an aligned monodomain. After alignment, the column axis is parallel to the shearing direction, i.e., the discotic molecules are standing perpendicular to the glass slide. The ionic conductivity parallel to the column axis is much higher than the ionic conductivity perpendicular to the column axis. The paraffinic continuum acts as an insulating sheet. The ionic conductivity is anisotropic in the columnar mesophase only, not in the isotropic liquid. The total ionic conductivity and the conduction anisotropy could be increased by doping the mesophase by the salt LiBF₄. This dopant has also a positive effect on the temperature range of the mesophase, i.e., the clearing point increases. It is assumed that the salt is incorporated in the ionic part of the mesomorphic material.

Kato and co-workers developed an anisotropic ionconductive material consisting of a conventional imidazolium ion liquid (215) and a hydroxyl-terminated liquid crystal (216).^{572,583,584} By the interaction between the ionic liquid and the hydroxyl groups the layered assembly is stabilized. Conductivity measurements on oriented monodomains showed that the anisotropy in the smectic B phase was higher than in the smectic A phase. The ordered packing of the ion-insulating mesogens in the smectic B phase leads to lower conductivity perpendicular to the layers. Kato, Ohno and co-workers have prepared a methacrylic acid monomer with an imidazolium and a mesogenic group attached to it via an alkyl spacer.⁵⁸⁵ In-situ polymerization of the oriented liquid-crystalline monomers was used to obtain liquid-crystalline polymers with macroscopically oriented nanostructures. Polymerization stabilizes the ionic layers formed by the monomer through self-assembly. Both the monomer and the polymer exhibit a smectic A phase. The polymer films with the monodomain structure has in the smectic A phase at 150 °C an ionic conductivity that is about 40 times higher than that of a polymer film with a polydomain structure at the same temperature. This shows that the boundaries in the randomly oriented polydomains disturb the high ion conduction. Nanostructured anisotropic ion-conductive films were obtained by insitu photopolymerization of a monomer consisting of a methacrylate polymerizable group, a tetra(oxyethylene) moiety as ion conducting part, and a mesogenic group that is responsible of self-organization and insulation (217).⁵⁸⁶ Photopolymerization was carried out on an aligned sample in the smectic A phase. Before polymerization, a complex was formed between the monomer and lithium triflate to introduce charge carriers in the system. The complex shows spontaneous homeotropic alignment on glass and ITO (indium tin oxide) substrates when cooled from the isotropic state to the smectic A phase. The macroscopic alignment of the molecules and subsequent stabilization of the monodomain by polymerization leads to a high anisotropy of the ionic conductivity. The ionic conductivity parallel to the smectic layers is larger by a factor of 4500 than the ionic conductivity perpendicular to the smectic layers.



The liquid-crystalline materials that were discussed in this section should not be confused with liquid crystals that show anisotropic electric conduction. The materials reviewed here exhibit electric conductivity thanks to ions as charge carriers. It is of course also possible to have conductive molecular materials in which electrons are the charge carriers. Liquid-crystalline bis(phthalocyaninato)lutetium(III) complexes are intrinsic molecular semiconductors.^{14,587,588} In these materials, the generation of charge carriers can be represented by the reaction AAA \Leftrightarrow A⁺A⁻A \Leftrightarrow free carriers, where A is the molecular unit. The ionized pair A⁺A⁻ is photochemically or thermally activated. The self-organization of the discotic phthalocyanine compounds into columnar stacks provides a one-dimensional pathway for charge transport.

9.2. Organized Reactions Media

Liquid crystals are anisotropic solvents and can be used as organized reaction media. Because of the orientation of the molecules dissolved in the liquid crystal, the regioselectivity and the chemoselectivity of organic reactions in liquid-crystalline solvents differ from those observed in conventional organic solvents.589,590 Most of the studies on organic reactions in liquid-crystalline solvents concern neutral liquid crystals. So far, only very few studies have considered the use of ionic liquid crystals as solvent for organic reactions. Lin and co-workers demonstrated the influence of the liquid-crystalline Nalkylimidazolium ionic liquids on the stereoselectivity of a Diels-Alder reaction.¹⁵⁸ A preference for the exo over the endo product was found for the cycloaddition of cyclopentadiene with diethyl malonate. Whereas in ethanol the exo/endo ratio was 12:88, in the ionic liquid crystal it was 54:46. The reaction conditions were controlled such that during the reaction the ionic liquid remained in the lamellar mesophase state.

9.3. Functional Nanostructured Materials from lonic Self-Assembly

Ionic self-assembly (ISA) is the coupling of structurally different building blocks by electrostatic interactions. One of the building blocks is often a cationic surfactant like a quaternary ammonium salt, while the other building block can be a negatively charged ionic dye, a polyelectrolyte, or a negatively charged metal complex. The use of ionic self-assembly for the synthesis of supramolecular and nanostructured materials has been reviewed in an excellent review by Faul and Antonietti.⁵⁹¹ Advantages of this method are the commercial availability of (relatively) cheap building blocks (cationic surfactants, dyes, polyelectrolytes, ...) and the simplicity of the synthesis (neat addition and cooperative stoichiometric precipitation of high purity products). The materials can be reprocessed by redissolution in an organic solvent or even in the liquid-crystalline state. Functional materials with interesting optical, electrical, magnetic, thermal, structural, or mechanical properties can be designed by a proper choice of the building blocks. ISA has to be differentiated from simple salt association. ISA is often accompanied by a cooperative binding mechanism in the sense that the first bonds stimulate further binding of charged molecules toward a final self-assembled structure. Of course, not all materials prepared by ISA exhibit liquidcrystalline behavior. The presence or absence of mesophases are largely determined by the type of cationic surfactant used. A rule of thumb is that quaternary ammonium salts with two long alkyl chains (e.g., dimethyldioctadecylammonium bromide) are a better choice than quaternary ammonium salts with one long alkyl chain (e.g., octadecyltrimethylammonium bromide) when one wants to obtain mesomorphic ionic self-assembled structures. Several examples of ionic liquid crystals prepared by the ISA method have been described in the different chapters above, e.g., perylene-based complexes,¹²² tricycloquinazoline-based complexes,¹²³ benzenehexacarboxvlic acid-based complexes,¹²¹ and the polyelectrolytesurfactant complexes (section 8.2).

10. Conclusions and Outlook

In this review, thermotropic ionic liquid crystals have been discussion and their relationship to ionic liquids has been revealed. The number of different classes of ionic liquid crystals is still rather limited, and the field has potential for a strong expansion. Much of the work has been restricted to investigation of the influence of the chain length on the thermal behavior of these ionic compounds, and less attention has been paid to systematic variation of the counterion and substitution patterns. The variation of the counterion is in most cases easier to perform than the variation of the substitution pattern. Introduction of different substituents on heterocyclic cores is synthetically a more demanding task but also a more challenging one. An interesting aspect of ionic liquid

crystals is their rich smectic polymorphism and the fact that the their ionic nature stabilizes uncommon mesophases such as the nematic columnar phase (N_{col}) . The highly ordered smectic mesophases are especially observed in cases in which a calamitic mesogenic group is connected by a flexible alkyl chain to the cationic organic group.^{159,196} On the other hand, the simple nematic phase is a very rare mesophase for ionic liquid crystals. A general feature of ionic liquid crystals is the strong tendency to show spontaneous homeotropic alignment, which can be observed by polarizing optical microscopy. The ionic crystals act as a surface treatment reagent that promotes homeotropic alignment. In the case of homeotropic alignment, shearing the two glass plates can induce birefringence. 592

Theories that can explain the influence of the anisotropic charge distribution on the mesophase stability of ionic liquid crystals are still lacking. The availability of such a theory could be a great addition for the rational design of ionic liquid crystals and for the occurrence of unexpected mesophases. The role of water molecules on the mesophase behavior is not fully understood yet. It is not always realized that water molecules have a profound influence on the thermal behavior of mesogenic salts. Therefore, future workers in the field should make all possible efforts to synthesize ionic liquid crystals that are free from water molecules (or from other solvent molecules).

To keep the attention of the scientific community, a research field needs to have some prospects for future applications. There would never have been such an interest in liquid crystals if the LCDs were not introduced on the market. The field of ionic liquids owes much of its interest to the possible applications of ionic liquids as an alternative for volatile organic solvents in industrial processes. It is unlikely that ionic liquid crystals will ever find application in displays. The conventional organic liquid crystals simply perform too well. On the other hand, anisotropic ionic conductivity can find applications in molecular electronics. The materials could also have potential as electrolytes in dye-sensitized solar cells (Grätzel cells).^{593,594} Thermotropic ionic liquid crystals can be used as ordered solvents or organized reaction media. In these anisotropic solvents other chemo- and regioselectivities besides those in conventional solvents can be obtained for several types of reactions.

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