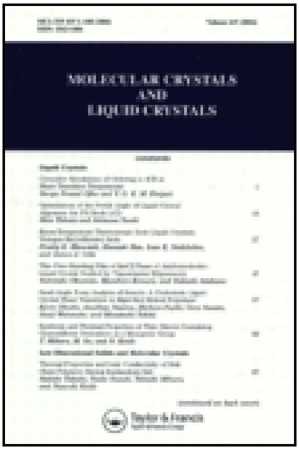

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Early History of Liquid Crystalline Compounds

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To cite this article: V. Vill (1992): Early History of Liquid Crystalline Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 213:1, 67-71

To link to this article: http://dx.doi.org/10.1080/10587259208028718

Mol. Cryst. Liq. Cryst., 1992, Vol. 213, pp. 67–71
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Printed in the United States of America

Early History of Liquid Crystalline Compounds

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(Received March 19, 1991; in final form July 17, 1991)

A short survey is given of the first thermotropic liquid crystals described in the literature. Magnesium myristate was the very first compound for which melting anomalies were reported, and thus the first liquid crystal. The first discotic liquid crystal was sodium diphenylacetate studied by Vorländer. His academic scholars were the first to observe liquid crystalline phases in oligomeric perhaps polymeric system.

Keywords: history of liquid crystals, agaric acid

INTRODUCTION

"Und doch sind die weichen Kristalle organischer Verbindungen die Wohnräume des Lebens. Ohne weiche Kristalle und Kolloide keine Lebewesen."[1]

Investigations with regard to the history of science use to be a privileged area for scientists richer in years of experience. In the area of liquid crystals this credit is certainly due to Kelker[2] who presented the scientists of the first hour to us. My personal approach is to contribute some remarks to the history of liquid crystals and these result from extended literature searches in connection with the establishment of a data bank[3] on liquid crystals. During these readings I came across some earlier papers of general interest, and in addition to the *persons*[2] of the first hour, emphasis here is on the *compounds* of the first hour.

The First Thermotropic Liquid Crystals

Generally the discovery of liquid crystals is dated back to the year 1888 when the botanist F. Reinitzer[4] observed the cloudy melting of the cholesteryl benzoate **1** and cholesteryl acetate. He donated these compounds to the physicist O. Lehmann[5] who described liquid crystals as a novel state of matter. Thus, the year 1888 may be correctly dated as the beginning of liquid crystalline scientific studies even though the phenomenon as such was documented earlier.

Already, in 1854, the physician Virchow[6,7] described the lyotropic liquid crystalline properties of myelin, and in 1861 Planer[8] observed the thermotropic cholesteric phase of cholesteryl chloride, however, without a correct interpretation of these observations. Eleven years later the fluorescence phenomenon in a cholesteryl amine-containing preparation was noted by Loebisch.[9]

The first description of a thermotropic liquid crystal is documented by Heintz[10,11] who as early as 1855 reported the stepwise melting of magnesium myristate **2**.

If one takes into account that the α-phase of lipids is to be regarded as a liquid crystalline phase, the early studies of mesophases date back to 1852 when Duffy detected the polymorphism of triglycerides.[12]

Obviously research on liquid crystals became possible after the fatty acids were obtained in a chemically pure state. In the beginning mesophases and lipids covered very closely related research areas. For instance, Vorländer studied both "the uniaxial arrangement of solid soft crystals and crystalline liquids" ("die einachsige Aufrichtung von festen weichen Kristallmassen und von kristallinen Flüssigkeiten"[1]).

The First Discotic Liquid Crystals

Research on discotic liquid crystals began in 1977 with the remarkable study of Chandrasekhar *et al.*[13] about hexa-substituted benzene derivatives such as **3**. But even in this class of compounds precursors can be traced in earlier reports. In 1935 Schadendorff and Verdino[14] gave evidence of a mesophase of 1,3,5-tris(cholesteryloxycarbonyloxy)benzene **4**, which later on was identified as a discotic mesophase.[15]

In another example, the mesophase of the disilanol **5** studied by Eaborn and Harshorne[16] in 1955 was later shown to be a discotic phase.[17]

As could have been almost expected, the first discotic liquid crystals were studied by Vorländer. Even though he could not positively answer the question whether star-like, cross-like or leaf-like molecules give rise to liquid crystalline phases,[18] he detected a mesophase for the sodium salt of diphenylacetic acid **6**,[19,20] which later could be assigned as hexagonal and thus discotic by Demus *et al.*[22]

Unknown up to date are the liquid-crystalline phases of Bis(heptaphenylcycloheptatrienes).[21]

Quite interesting compounds with potential mesogenic properties are the tannins, the gallic acid esters of glucose. Already in the first quarter of this century these compounds were reported to exhibit melting anomalies.[23,24,25] Further, natural products with discotic potential are at hand in dialkylated carbohydrate derivatives such as glycosyl glycerides,[26] cerebrosides, sulfatides, and phospholipids.

Liquid Crystalline Polyols

The field of carbohydrate chemistry became involved in liquid crystalline properties of sugar derivatives since about the eighties.[27] However, Emil Fischer[28] observed and described the double melting of hexadecyl β-D-glucopyranoside **7** as early as 1911. One year later Salway[29] proved Fischer's observation to be right. In addition, he pointed to melting anomalies of the steryl glycosides. In fact, there have been only a few studies with regard to the mesogenic potential of this class of compounds[30,31] since then.

However, long before Fischer, Berthelot[32] was in contact with liquid crystalline carbohydrate derivatives when in 1855 he studied monoacylated mannitol and further polyols. He described mannitol oleate as "cireuse, très-fusible en un liquide visqueux."[32] Closely related to the polyols is agaric acid. The mesophase of this acid, a S_A phase,[31] was first described by Gaubert.[33]

Polymeric Liquid Crystals

"What happens with the molecules if they are further and further elongated? Will the liquid crystalline property eventually disappear? Following my experience a limit for such a state given by elongation of the chains is not at hand. However, it may happen that the compounds no longer melt without decomposition, or cannot be observed under the microscope" (Was geschieht mit den Molekülen, wenn man sie immer weiter und weiter verlängert? Wird der kr. fl. Zustand schließlich verschwinden? Nach meinen Erfahrungen ist eine Grenze für diesen Zustand bei der Verlängerung der Ketten nicht vorhanden, es sei den, dass schliesslich die Substanzen nicht mehr unzersetzt schmelzen und nicht mehr zu mikroskopieren sind."[18])

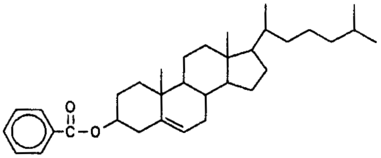
Exactly this gives evidence of the experience obtained with all polymers studied in Halle by Vorländer *et al.* in the thirties. Among these were condensation products of aromatic dialdehydes and aromatic diamines[34] such as **8** or cyclic ketones[35] **9**. Vorländer called these nonmelting stiff main chain polymers "supracrystalline" compounds.

In 1924 Horbach[36] studied oligomers of *p*-hydroxybenzoic acid which at high temperature were liquid crystalline. However, in most cases the clearing points could not be determined owing to decomposition or polymerization on heating. It is interesting to note that he obtained a tough laquer by annealing the liquid crystalline phase of "vanilloyl-di-oxybenzoic acid" **10**. Obviously this represented the properties of the mesophase frozen in an oligomer (or polymer ?) melt, and a potential candidate for nematic main chain polymers by polycondensation was obtained.

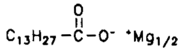
In 1938 Lorand[37] observed softening points by liquid-crystalline alkylcelluloses.[38]

The systematic studies of melting liquid crystalline polymers did not commence before the end of the seventies.[39,40,41,42]

The very first liquid crystals most likely date back to the Phoenicians, Sumerers, Egyptians and Israelis, who, some thousands of years ago, already used soaps.[43,44] Their predominant interest did not concentrate on their mesomorphic, but on their surfactant properties: "Though you wash with soda and use soap lavishly, the stain of your sin is still there for me to see." (Jer. 2,22).[45] However, crystallographic studies and findings from this time were not reported. This lack of information was compensated much later and again by Vorländer[1]: " . . . in crystallographic assignments soaps would be best described as solid soft double refracting biaxially and monoaxially erected crystals or unicells in manyfold intergrowth and disorder" (" . . . kristallographisch würde man nur angeben können, dass die Seife ein Gemisch von festen weichen doppelbrechenden zweiachsigen und einachsig aufgerichteten Kristallen oder Mizellen in mannigfacher Verwachsung und Verzerrung enthält").

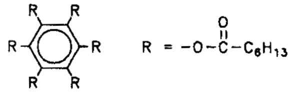


1 Cr 151 X 178.5 I [4]

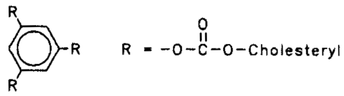


$C_{13}H_{27}-\overset{O}{\overset{\|}{C}}-O^{-}\ {}^{+}Mg_{1/2}$

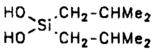
2 Cr 140 X >150 Z [10]



3 Cr 80.2 D 86.2 I [13]
Cr 85.5 I [46]

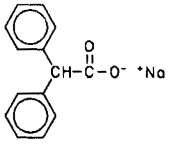


4 Cr 143 X 161 I [14]
Cr 156.9 D 165.3 I [15]

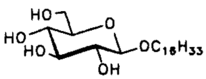


$\begin{matrix}HO \\ HO\end{matrix}\!\!>\!Si\!<\!\begin{matrix}CH_2\text{-}CHMe_2 \\ CH_2\text{-}CHMe_2\end{matrix}$

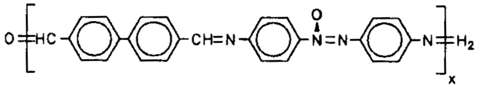
5 Cr 89.5 X 101.5 I [16]
Cr 88.4 D 97.7 I [17]



6 Cr ? X ? I [19]
Cr 249 D 316 I [22]



7 Cr 78 X 145 I [28]
Cr 78 X 145 I [29]
Cr 81.5 S_A 147.5 I [31]



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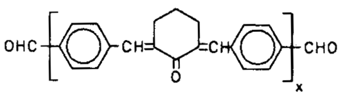

9

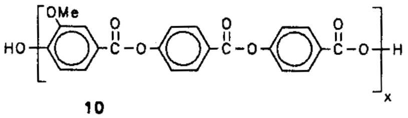

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FIGURE 1

Acknowledgments

Support of the data bank programme by the Bundesministerium für Forschung und Technologie and the Springer Publishing Company is gratefully acknowledged. Prof. J. Thiem and Mrs. R. Poehls are thanked for their kind help, and Dr. N. Weber for a sample of hexadecyl glucopyranoside.

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