Liquid Crystals

DOI: 10.1002/anie.201301457

125 Years of Liquid Crystals—A Scientific Revolution in the Home**

Thomas Geelhaar, Klaus Griesar, and Bernd Reckmann*

displays · history of science · industrial chemistry · liquid crystals · materials science

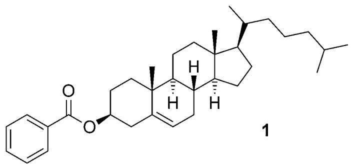
In 2013 *Angewandte Chemie* celebrates its 125th birthday. It is also the 125th year since liquid crystals were first discovered. Modern life would be unimaginable without liquid crystals because they have found their way into so many products we use today. Hardly any other high-tech material has become so widespread so quickly. The millions of people owning a tablet computer enjoy its brilliant display without as much as an inkling of the liquid crystals between the glass plates and polarizers.

What is the story behind the discovery of liquid crystals in 1888? At that time microscopes were widely used in scientific research, notably in botany and histology. And polarizing microscopes were frequently used in mineralogy and crystallography.[1] Not only scientists, however, were showing an interest in microscopy: the microscopic study of radiolaria (protozoa that produce intricate mineral skeletons) and diatoms (algae with a cell wall made of silica) led Ernst Haeckel to publish *Art Forms of Nature*, a book with over 100 detailed, multicolor illustrations of animals and sea creatures which influenced in particular the Art Nouveau movement and inspired the optical instrument manufacturer Johann Diedrich Möller to prepare diatom slides.[2] Salon evenings provided a great opportunity for viewing such microscope slides and for discussing, for instance, the bridge between living and nonliving matter.

1. 1888–1913: Discovery

In 1888 at the German Technical University in Prague Friedrich Reinitzer (Figure 1), Professor of Botany and Technical Microscopy, was investigating cholesterol derivatives: initially cholesterol[3] itself, which he had extracted from carrots, and subsequently also cholesteryl benzoate.[4] Reinitzer measured the melting point of cholesteryl benzoate (**1**) at 145.5 °C; he found a second melting point, however, at 178.5 °C and between the two was a milky liquid phase. Above 178.5 °C the phase was clear.

Figure 1. Friedrich Reinitzer (1857–1927). Source: Merck (with kind permission from Dr. Sigrid Reinitzer, Graz, Gero Reinitzer, Vienna, and Prof. Dr. Heimo Reinitzer, Hamburg).



1

Under the polarizing microscope he observed distinct violet and blue color phenomena at both phase transitions. Having made similar observations with a further derivative, cholesteryl acetate, which has a monotropic cholesteric phase, he contacted physicist Otto Lehmann (Figure 2), an expert in the physical isomerism of crystals and lecturer first in Aachen, then in Dresden, and from 1889 in Karlsruhe. Lehmann had a polarizing microscope with a hot stage and was thus able to investigate more precisely than Reinitzer. The very lively correspondence between Lehmann and Reinitzer[5] resulted in 1889 in Lehmann's publication *Über fließende Kristalle*.[6] Reinitzer, the biologist, therefore is seen as the discoverer of liquid crystals; Lehmann, the physicist, is hailed as the founder of liquid crystal research.

[*] Dr. T. Geelhaar, Prof. Dr. K. Griesar, Dr. B. Reckmann
Technology Office Chemicals, Merck KGaA
Frankfurter Strasse 250, 64293 Darmstadt (Germany)
E-mail: thomas.geelhaar@merckgroup.com
Homepage: http://www.merckgroup.com

[**] Chapter 6 is part of the plenary lecture held by Bernd Reckmann: "Innovations in Chemistry". Wissenschaftsforum Chemie 2013, Darmstadt.

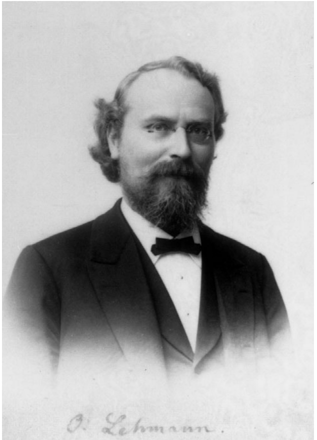


Figure 2. Otto Lehmann (1855–1922). Source: Merck (with kind permission from the Archive of the Karlsruhe Institute for Technology, Karlsruhe).

Figure 3. First edition of the book by Carl Krauch, *Die Prüfung chemischer Reagenzien auf Reinheit*, published in 1888. Ref. [7] (source: Merck).

At the time doubts began to emerge about Reinitzer's and Lehmann's observations and explanations and, in particular, the purity of the liquid crystalline substances they used was questioned.

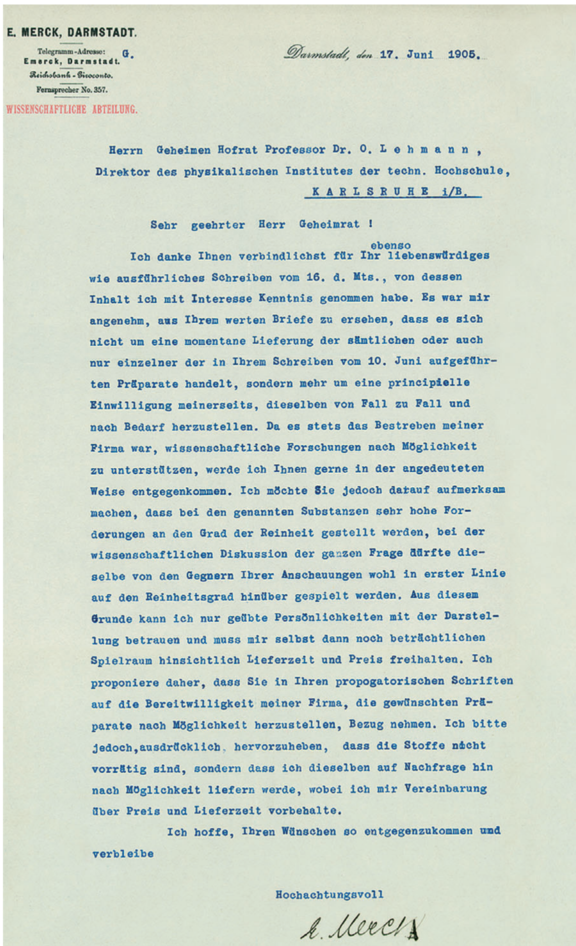
Heinrich Emanuel Merck, founder of Merck, the oldest chemical-pharmaceutical company in the world, took over the Engel-Apotheke in Darmstadt in 1816 as pharmacist, and in 1827 commenced the industrial production of alkaloids, the quality of which he vouched for to his customers in 1851. In the year in which Reinitzer discovered liquid crystals, Darmstadt-based Merck for the first time guaranteed the purity of its substances by establishing defined specifications. In the same year Merck chemist Carl Krauch published the first standard work on chemical analysis (Figure 3) entitled *Die Prüfung chemischer Reagenzien auf Reinheit*.[7]

Reinitzer's and Lehmann's work created a demand for liquid crystalline substances with cholesteric and nematic phases, which Merck was able to meet by synthesizing substances in the required purity. In 1904 this class of substances was already listed in a company brochure for scientific studies; the substances included cholesteryl acetate, cholesteryl benzoate, *p*-azoxybenzoic ester, *p*-azoxyphenetol, and *p*-azoxyanisole. Figures 4 and 5 depict correspondence between Merck and Lehmann in 1905 and a Merck advertisement dating from 1907 showing Lehmann's polarizing microscope. In commemoration of Krauch's standard work of 1888, Merck in 1988 inaugurated the Heinrich Emanuel Merck Award for Analytical Science which is granted every two years to promising young scientists. Therefore, we are also looking back 125 years to the publication of Krauch's seminal work.

On the Ascension Day weekend of 1905 physical chemists in Germany met at the annual convention of the German Bunsen Society in Karlsruhe to discuss, among other things, the results of Lehmann's work. There were proponents and opponents when it came to Lehmann's "liquid crystals", with Tammann being the most sceptical contributor: "*Soft crystals definitely do exist, flowing crystals may exist, but liquid crystals definitely cannot exist*".[8] The discussion leader van't Hoff gave Lehmann no opportunity to defend his position. At the next meeting of the Standing Committee of the Bunsen Society it was decided to establish a commission to clarify the contentious issues, to be chaired by van't Hoff and to which Lehmann was also invited. His 1906 pamphlet to the commission members lists the unresolved questions:[5]

"…*To avoid being deceived by characteristic refraction (within the polarizing microscope) it is also necessary to have some experience in the field of crystal optics (and of theoretical optics in general). An assessment of the state of aggregation must be founded on the precise definition of the terms that are essential to theoretical mechanics and molecular physics. The decision whether assignment to the existing crystal system is possible based on vectorial properties falls within the realm of*

Thomas Geelhaar (born 1957) studied chemistry at the University of Mainz from 1975 to 1981 and received his PhD in physical chemistry there in 1983 under the direction of Prof. Wolfgang Liptay. In 1984, he started working in liquid crystal research at Merck in Darmstadt and in 1997 became General Manager Marketing & Sales in the Liquid Crystals Division. In 2000 he was appointed as Head of the Liquid Crystals Division in Japan. From 2003 to 2007 he was Vice President of Liquid Crystal Research and New Technologies Chemicals as well as Managing Director of Merck OLED Materials GmbH since 2005. In 2007 he was appointed Chief Technology Officer Chemicals and Senior Vice President. Since 2007 he has been on the Executive Board of the GDCh and has been Treasurer of the GDCh since 2010. In 2012, he became a member of the Editorial Board of Angewandte Chemie.


E. MERCK, DARMSTADT.
Telegramm-Adresse: Emerck, Darmstadt. G.
Reichsbank-Giroconto.
Fernsprecher No. 357.
WISSENSCHAFTLICHE ABTEILUNG.

Darmstadt, den 17. Juni 1905.

Herrn Geheimen Hofrat Professor Dr. O. L e h m a n n ,
Direktor des physikalischen Institutes der techn. Hochschule,
K A R L S R U H E i/B.

Sehr geehrter Herr Geheimrat !

Ich danke Ihnen verbindlichst für Ihr ebenso liebenswürdiges wie ausführliches Schreiben vom 16. d. Mts., von dessen Inhalt ich mit Interesse Kenntnis genommen habe. Es war mir angenehm, aus Ihrem werten Briefe zu ersehen, dass es sich nicht um eine momentane Lieferung der sämtlichen oder auch nur einzelner der in Ihrem Schreiben vom 10. Juni aufgeführten Präparate handelt, sondern mehr um eine principielle Einwilligung meinerseits, dieselben von Fall zu Fall und nach Bedarf herzustellen. Da es stets das Bestreben meiner Firma war, wissenschaftliche Forschungen nach Möglichkeit zu unterstützen, werde ich Ihnen gerne in der angedeuteten Weise entgegenkommen. Ich möchte Sie jedoch darauf aufmerksam machen, dass bei den genannten Substanzen sehr hohe Forderungen an den Grad der Reinheit gestellt werden, bei der wissenschaftlichen Diskussion der ganzen Frage dürfte dieselbe von den Gegnern Ihrer Anschauungen wohl in erster Linie auf den Reinheitsgrad hinüber gespielt werden. Aus diesem Grunde kann ich nur geübte Persönlichkeiten mit der Darstellung betrauen und muss mir selbst dann noch beträchtlichen Spielraum hinsichtlich Lieferzeit und Preis freihalten. Ich proponiere daher, dass Sie in Ihren propogatorischen Schriften auf die Bereitwilligkeit meiner Firma, die gewünschten Präparate nach Möglichkeit herzustellen, Bezug nehmen. Ich bitte jedoch,ausdrücklich, hervorzuheben, dass die Stoffe nicht vorrätig sind, sondern dass ich dieselben auf Nachfrage hin nach Möglichkeit liefern werde, wobei ich mir Vereinbarung über Preis und Lieferzeit vorbehalte.

Ich hoffe, Ihren Wünschen so entgegenzukommen und verbleibe

Hochachtungsvoll

E. Merck

Figure 4. Merck's letter of 1905 to Otto Lehmann with the promise of scientific support (source: Merck).

Figure 5. Otto Lehmann's polarizing microscope was featured in Merck's advertisement (1907) for liquid crystals and other Merck products (source: Merck).

crystallography; the study of magnetic properties, within that of the electrician. The fundamental question as to whether the preparations can be seen as entities in the chemical sense can definitely be answered only by a chemist; the study of scalar properties and thermodynamic relations, on the other hand, is a matter for a physical chemist. Whether the characteristic processes observed in apparently living crystals not only outwardly resemble the corresponding processes in the lowest forms of life but are also based on a real relationship of the physical forces they entail are questions which the physiologist and biologist have to decide. The physicist's interest is mainly shackled by the notion that the deduction of those processes from what is already known seems impossible…"

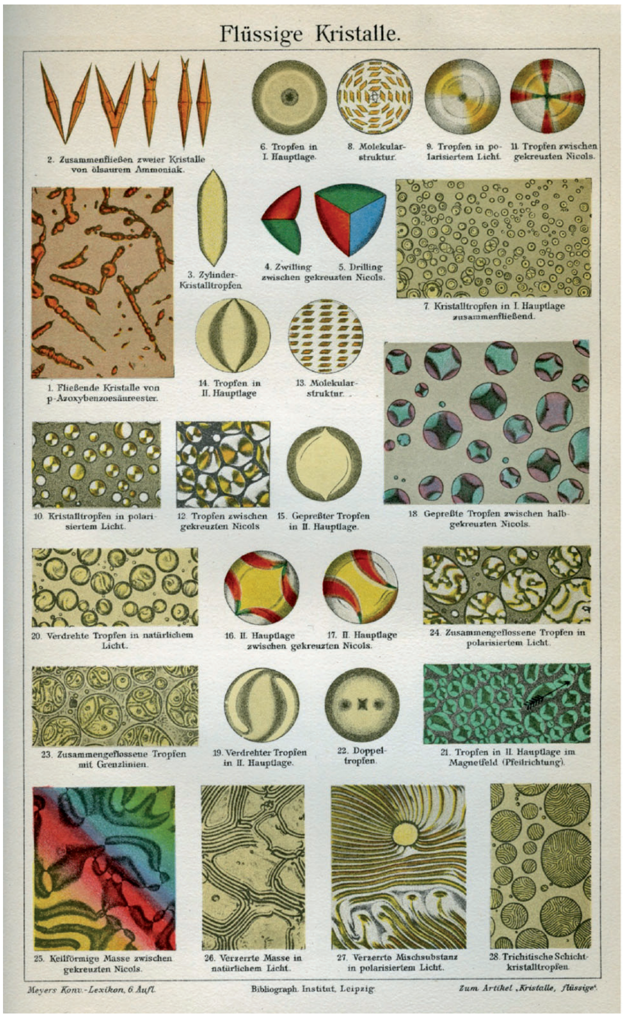
Unfortunately, the commission set up by the Bunsen Society also failed to reach a conclusion. Lehmann's lecture on "Liquid and apparently living crystals" at the Natural Scientists' and Physicians' Meeting in Stuttgart in 1906, which was covered at length in *Angewandte Chemie*,[9] clearly presented the controversy surrounding "living crystals" (Figure 6: Haeckel's "Kristallseelen")[10] from the perspective of the biologist Haeckel but, despite the interdisciplinary discussion between biologists, physicists, and chemists, the only conclusion was that it was unclear what the outcome of the controversy might be. It is said that Lehmann, following publication of his paper "Liquid crystals and their (apparent) vital properties" was asked, "*My dear colleague, do they eat as well?*"[5]

At that time Daniel Vorländer, in Halle, was one of the leading synthetic chemists. In 1906 he described a series of "crystalline-liquid" azoxybenzoates.[11] Through variation of substituents and investigation of homologous series of rod-shaped molecules he proposed the first structure–property correlations for the occurrence of birefringent crystalline-liquid phases, which we today refer to as nematic.

In 1911 French mineralogist Charles-Victor Mauguin investigated the orientation of liquid crystalline *p*-azoxyanisole in a magnetic field and was able to determine a high birefringence in uniformly homogeneously oriented samples of larger layer thickness.[12] With this he had started the systematic measurement of anisotropic physical properties of liquid crystals.

It is clear then that the first 25 years in the study of liquid crystals were characterized, on the one hand, by interdisciplinary research and, on the other, by debates between the individual research groups attempting to explain the phenomena. The dispute concerning the discovery of liquid crystals is reminiscent of similar confrontations which Max Planck experienced at the same time concerning his quantum theory. Planck wrote:[13]

"*…A new scientific truth does not triumph by convincing its opponents and making them see the light. It rarely happens that Saul becomes Paul. What does happen is that its opponents gradually die out and that the growing generation is familiarized with the idea from the beginning…*"



Ernst Haeckel wrote in *Kristallseelen ("Crystal souls")* in 1917, e.g. to explain Figure 2 (top left):

Copulation of two living spindle crystals of ammonium oleate. If two such spindle-shaped "liquid crystals" randomly touch one another, they lay one next to the other and flow completely together; on the right is the new "double pyramid" which is formed.

And on the work of Otto Lehmann:

The history of his epoch-making discovery, recounted by Otto Lehmann himself in the book, Die scheinbar lebenden Kristalle, is very informative for understanding the obstacles which dogmatic tradition has laid in the way of the recognition and dissemination of profound changes. The "liquid, apparently living crystals" required a full thirty years before they were able to capture the general and worthy recognition of the immediately interested "specialists" among the physicists, chemists and mineralogists and be included in the textbooks; even today they are ignored by certain prominent physicists.

And on the vital signs of liquid crystals:

Growth: Their most important living activity ... is their growth.
Nourishment: In order for the liquid crystal to grow, it must be provided with liquid nutritional material. It can, however, "eat" directly. The stronger stable form consumes the labile form and grows at its expense.
Copulation: In many liquid crystals two individuals flow together as soon as they come in contact with one another; the doubled individual immediately assumes the form of two paired individuals again.
Regeneration: Many crystals, both solid and liquid, have the ability to heal damage and replace missing parts ...
Motion: Among the most conspicuous phenomena of life for the liquid crystals are the lively movements which take place at definite temperatures in the mother liquor. They are linked with significant changes in form and with copulation phenomena. ... The double droplets which have coalesced can form rodlets like bacteria and extend to form long "snake-like bodies". ... The swarming of these nematode-like liquid crystals is like that of infusoria, which move tumultuously in a water droplet.
Sensation: The unbiased comparison of the different states of the liquid crystals and of the changes which they undergo in their vital activities, especially their critical comparison with the lowest organisms, leads us to the conviction that the "living substance" of the former is just as endowed with unconscious sensitivity as is the plasma of the latter. Especially conspicuous here is their correspondence with the radiolaria.

Figure 6. "Liquid crystals" chart published in *Meyers Großes Konversations-Lexikon*, 6th Edition, Bibliographisches Institut, Leipzig, 1905, Volume 11, page 708 to accompany the article "Kristalle, flüssige" by Otto Lehmann, and Ernst Haeckel's explanation in *Kristallseelen* ("*Crystal souls*") in 1917. Ref. [10] (source: http://caliban.mpiz-koeln.mpg.de/haeckel/kristallseelen/index.html in http://www.BioLib.de).

2. 1914–1938: Paradigm Shift

While Haeckel and Lehmann from 1917 to 1919 were still discussing the question of whether liquid crystals are in actual fact "living crystals"—Haeckel indeed continued to be convinced that, with his "Kristallseelen" ("Crystal souls"), he had managed to discover the long sought-after link between nonliving and living matter—science in Europe was starting to focus on the unexplained phenomenon (Figure 7).

An extremely important contribution to the understanding of liquid crystals was made by French mineralogist and crystallographer Georges Friedel,[14] Professor for Geology at the University of Strasbourg, who, in 1922, published a 200 page review article on the "mesomorphic states of matter", excerpts of which were published in English in the book *Crystals that flow* by T. Sluckin, D. Dunmur, and H. Stegemeyer.[15] In it Friedel criticized the German physicists, who for more than 30 years had been unable to explain the liquid crystalline state. In his work he described 42 liquid crystalline compounds, and characterized smectic and nematic as well as cholesteric phases through their textures in homogeneous and homeotropic orientations. He also investigated mixtures of liquid crystals and their phase diagrams

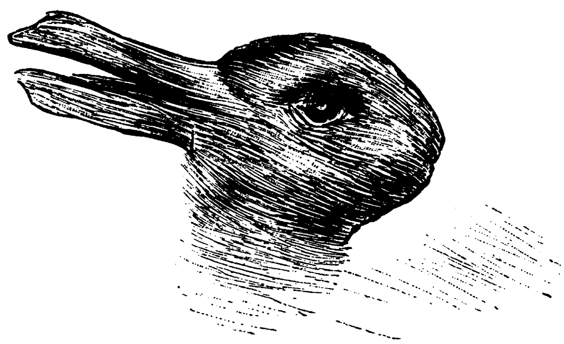


Figure 7. *Duck or rabbit?* Thomas Kuhn (Ref. [59]) used this optical illusion to highlight how a scientific revolution can suddenly alter a scientist's perspective (source: http://digi.ub.uni-heidelberg.de/diglit/fb97/0147, from 1892, Wikimedia Commons, Public Domain).

and explained the transitions between the mesophases when liquid crystalline substances and mixtures are heated.

The behavior of liquid crystals, in particular their orientation in fields, was described by Russian physicist Vsevolod Konstantinovich Freedericksz in 1927.[15] His theory explains both the parallel alignment of liquid crystals on surfaces in magnetic and electrical fields as a result of their anisotropic diamagnetic and dielectric properties as well as their reorientation with increasing field strength above a certain threshold; the transition is named after him, the Freedericksz effect or Freedericksz threshold, and is applied in modern-day liquid crystal displays (LCDs).

The theory of the elastic properties of liquid crystals was developed by Swedish physicist Carl Wilhelm Oseen in 1933; he delivered a significant contribution to the understanding of liquid crystals through his formulation of the elastic free energy based on the elastic constants.[16]

Unfortunately, neither Oseen nor Freedericksz were able to attend the first major discussion meeting of the Faraday Society in 1933 in London entitled "Liquid Crystals and Anisotropic Melts". Friedel died that same year. Even 50 years after their discovery, the properties of liquid crystals could be described and partly explained in theory, but a complete theory was still lacking. Daniel Vorländer said in 1924 that he could see "*no possible technical application for liquid crystals…*"[17]

3. 1939–1963: Research Revival

There were difficulties in preparing uniformly well-oriented samples of liquid crystalline substances suitable for examination under the microscope. French mineralogist Pierre Chatelain was the first to investigate systematically, in 1944, the influence of surface substrate treatment methods, such as rubbing or cleaning, on liquid crystal orientation.[18] The fact that the glass substrates were cleaned was just as decisive as the material (paper, wall, velvet) used for rubbing, the force applied during rubbing, and the number of rubbing operations. Even today the rubbing of polyimide-coated glass substrates with velvet rollers plays an important role in the manufacture of liquid crystal displays.

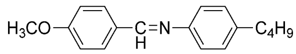
After the Second World War the highly acclaimed review article "The mesomorphic state—liquid crystals" by Glenn H. Brown, which appeared in 1957 in *Chemical Reviews*, breathed new life into liquid crystal research—now also in the USA.[19]

The first applications of liquid crystals came about as a result of research by James Fergason in the Westinghouse Research Labs in Pennsylvania. He used cholesteric liquid crystals for temperature indication and filed a patent application for this in 1958.[20] Therefore, the first practical application of liquid crystals was the use of cholesteric liquid crystals as temperature indicators in the nondestructive testing of materials and in medical diagnostics.

A refined theoretical description of the properties of nematic liquid crystals, the Maier–Saupe theory, was proposed in 1958. The intermolecular interactions are described here in terms of molecular field theory, and the temperature dependence of the order parameter can therefore be explained.[21] Alfred Saupe in Freiburg performed UV and later NMR spectroscopic investigations in liquid crystalline phases. By means of the orientation of the molecules in the nematic phase the determination of bond angles and bond lengths was also possible.

4. 1963–1988: Discovery and Application

In the 1960s Glenn H. Brown of Kent State University founded the Liquid Crystal Institute there, which hosted the first two international liquid crystal conferences in 1965 and 1968, at which the first applications of liquid crystals were discussed. George Heilmeier of the Radio Corporation of America (RCA) had just published his paper on the first electrooptic displays. With the first seven-segment displays based on the principle of dynamic scattering (DSM), Heilmeier developed the first liquid crystal displays using Schiff bases **2** with negative dielectric anisotropy.[22] For his work he received the Kyoto Award in 2005.



2

Heilmeier discovered a further interesting electrooptic effect when he doped a benzoate exhibiting a positive dielectric anisotropy with a dichroic dye and thus invented the guest–host cell.[23]

This discovery in 1968 also marked the start of liquid crystal research at Merck led by Ludwig Pohl (Figure 8) and

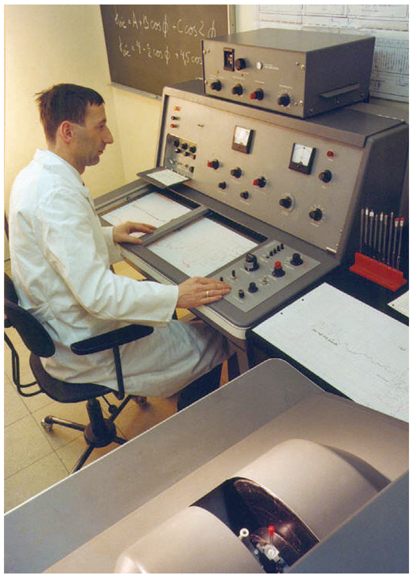
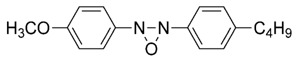


Figure 8. Ludwig Pohl in 1968 (source: Merck).

Bruno Hampel in the Central Analytical Laboratory and Ralf Steinsträsser and Dietrich Erdmann in the Chemical Research Department.[24] The first products were nematic solvents for NMR spectroscopy as well as the liquid crystal mixture Nematic Phase IV based on *p*-azoxybenzenes **3**[25] which was developed for use in segment displays utilizing the DSM effect. Other chemical companies, too, had recognized the potential of liquid crystals, and in 1969 Hans Kelker of Hoechst, for instance, developed liquid crystal mixtures for DSM-based segment displays using MBBA homologues **2** (*N*-(*p*-methoxybenzylidene)-*p*-*n*-butylanilines).[26]

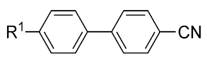


3

As early as 1971 Hoechst, with its advertising slogan "What's still stopping you from developing the flat TV screen?", provoked legal steps by television manufacturers who saw their business in traditional CRT (cathode ray tube)-based TV sets under threat. Liquid crystal displays were first used in pocket calculators produced by Sharp in 1973. Characteristic of these were their yellowish displays, as the *p*-azoxybenzenes used absorbed in visible light and had to be protected by a filter.

A decisive breakthrough came at the end of 1970 when Wolfgang Helfrich and Martin Schadt developed the twisted nematic (TN) mode at Hoffmann-La Roche.[27] Almost simultaneously, however, James Fergason of Kent State University announced the discovery in 1971 of the TN cell. In the TN cell, nematic liquid crystals exhibiting a positive dielectric anisotropy sandwiched between rubbed glass substrates switch from a homogeneous orientation with a 90° twist upon application of a small voltage at a perpendicular orientation. The liquid crystal molecules align along the electric field, resulting in a significant electrooptic effect. A further effect—this time using nematic liquid crystals with negative dielectric anisotropy—was described in the same year by Manfred Schiekel and Kurt Fahrenschon at AEG-Telefunken. The effect is known as the DAP (deformation of aligned phases) or the VA (vertically aligned) effect.[28] Here, a homeotropic orientation is changed to a homogeneous orientation through application of a voltage.

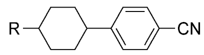
Following these basic innovations the challenge was now for the chemists to develop stable liquid crystals. Neither hydrolysis-sensitive Schiff bases nor light-sensitive *p*-azoxybenzenes were stable enough in the long term for practical application. The development of the cyanobiphenyls **4** by George W. Gray in 1973 at Hull University for the first time provided stable liquid crystals for TN displays, these were then sold by BDH Chemicals in Poole and Hoffmann-La Roche in Basel.[29]



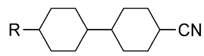
4

In the previous year Merck had taken over BDH Chemicals, and close collaboration began between researchers at Merck in Darmstadt, at BDH in Poole, at Hull University, and at the Royal Signals and Radar Establishment (RSRE) in Malvern. The first product using an LCD based on TN technology was a quartz watch in 1973 from Seiko Epson.

More detailed investigation, by C. H. Gooch and H. A. Tarry in 1975, regarding the transmission of a TN cell as a function of retardation (the product of layer thickness and birefringence), resulted in optimum contrast values at defined minima of the so-called Gooch–Tarry transmission curve.[30] The hunt was then on for liquid crystals exhibiting smaller birefringence than the previously established biphenyls. In 1975 Dietrich Demus had already produced cyclohexanecarboxylates in Halle,[31] but the actual breakthrough came in 1976 with the synthesis of cyanophenylcyclohexanes **5** and cyanobicyclohexanes **6** by Rudolf Eidenschink at Merck (Figure 9).[32]



5



6

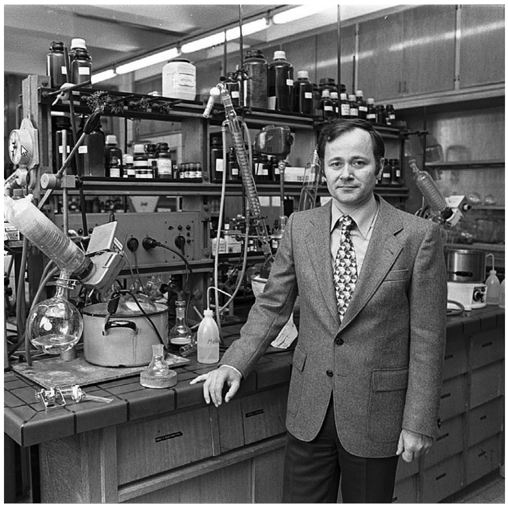


Figure 9. Rudolf Eidenschink (1938–2012) in 1978 (source: Merck).

Only with the advent of these materials was it possible to produce TN LCDs offering a number of advantages in the so-called first minimum of the Gooch–Tarry transmission curve, such as improved viewing angle dependence of contrast and fewer interference colors as long as certain retardation values are adhered to. One invention by Merck researchers Ludwig Pohl, Rudolf Eidenschink, Fernando del Pino, and Georg Weber in 1980 as a result of these considerations was licensed as the so-called viewing angle independent panel (VIP) in the 1990s to all TFT LCD manufacturers.[33]

French solid-state physicist Pierre-Gilles de Gennes (Figure 10) was the first to provide a full description, in 1971 in Orsay, of the free energy of liquid crystals through introduction of the order parameter tensor in the Landau–de-Gennes theory, which also explained the phase transitions.[34] Proceeding from his investigations into order phenomena in simple systems such as superconductors, he was also able to describe more complex systems such as liquid crystals, and for his work he was awarded the 1991 Nobel Prize in Physics—more than 100 years after Reinitzer's discovery.

Also in Orsay, American physicist Robert B. Meyer achieved a further breakthrough in 1975 with his prediction of ferroelectricity in chiral smectic C phases and demonstrated this with Schiff base **7**.[35] Then in 1980 Noel Clark and Sven Lagerwall were able, in an experimental setup using **7** in very thin layers, to achieve in the ferroelectric chiral smectic C

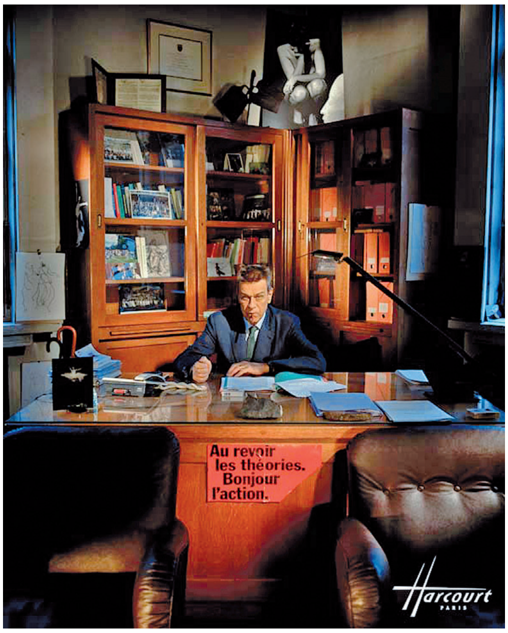
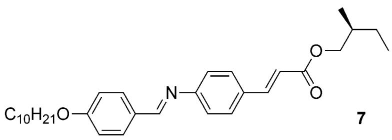


Figure 10. Winner of the 1991 Nobel Prize in Physics, Pierre Gilles de Gennes (1932–2007). (Source: Studio Harcourt Paris, Wikimedia Commons).

phase, a bistable electrooptic effect leading to switching times of microseconds. This was an improvement of several orders of magnitude compared to switching times of several milliseconds in TN cells.[36]

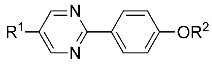


7

In the 1970s, liquid crystalline polymers and low-molecular-weight liquid crystals attracted the interest of several research groups. In 1978 in Mainz, Helmut Ringsdorf and Heino Finkelmann introduced spacer groups between the polymer main chain and the mesogenic side groups.[37] In the 1980s, attempts were made with polymer-dispersed liquid crystals (PDLC) to discover new applications for liquid crystals in switchable glass panels and windows; however, the technology did not catch on and remained limited to just a small number of applications such as internal glass walls (such as those used in German ICE high-speed trains) or the switchable PDLC glass roof (as in the Maybach luxury car).

In the 1980s, LCD technology continued to develop: progressing from their use in simple liquid crystal segment displays to the monochrome passive matrix LCD, used first in the Japanese word processors and subsequently in the first laptop computers. Along this line, matrix LCD addressing was developed, which required liquid crystals with special elastic properties; phenylpyrimidines **8**, in particular, were found to be suitable for this purpose.

This technology, however, was not suitable for the development of larger displays with more than 120 lines. These only came following their invention by Terry Scheffer



8

and Jürgen Nehring of the BBC company in Switzerland in 1984. They developed the super birefringence effect (SBE) mode, in which the twist is not 90° as in the TN cell but 270°.[38] This was the starting point in the 1980s and 1990s for the development of the super twisted nematic (STN) display, which found widespread use first in laptop computers and then in cell phones. For this application Hoffmann-La Roche alkenylphenylcyclohexanes, which have favorable elastic properties owing to their alkenyl side chains.[39]

The next challenge for chemists was then to develop liquid crystals with negative dielectric anisotropy, which were needed for VA or ECB (electrically controlled birefringence) displays as well as for FLC (ferroelectric liquid crystal) displays. Research scientists at Merck developed a wide range of 2,3-difluorobenzene derivatives, which were presented at the International Liquid Crystal Conference in Freiburg in 1988.[40] This provided the foundation for the subsequent success of VA displays. At this time both Canon with their development of the FLC display and Stanley with their development of the color super homeotropic (CSH) display failed to achieve any technical or commercial breakthroughs.

In the fall of 1988, Sharp achieved a big-bang moment for color LCDs[41] at a display conference in the USA when they presented their 14″ TFT (thin film transistor) LCD prototype. Of course, proponents of the established cathode ray tube technology expressed doubt as to whether the Japanese TFT developers would ever succeed in manufacturing the display, which was controlled by a matrix of 640×480 thin-film transistors, with just a limited number of pixels defects. Even at the end of the 1980s, it was still totally uncertain whether the STN displays or the TFT displays would prevail. At Merck the derisive term “Überflüssige Kristalle” (superfluous crystals) was still being used in reference to “Flüssige Kristalle” (liquid crystals), because after 20 years' research at Merck the modest sales volume of these products did not seem to justify the expense of maintaining a team of 80 chemists, physicists, and technicans. But whoever had seen the first Sharp TFT LCD display in 1988 was convinced of the possibility of producing a wall-mounted screen and had faith in extending and actively exploiting the most important success factors of the day. Interdisciplinary collaboration, local cooperation with the Japanese display manufacturers, and an unbiased technological approach to material development for all promising liquid display modes were key to the subsequent success of Merck.

5. 1989–2013: Success and Recognition

The breakthrough in the use of liquid crystals came with the success, at the beginning of the 1990s, of notebook PCs, which were possible thanks to LCDs. Initially in monochrome but very soon in color, the STN displays prevailed in the first half of the 1990s, to be superseded in the second half of the decade by TN TFT displays (Figure 11).[42]

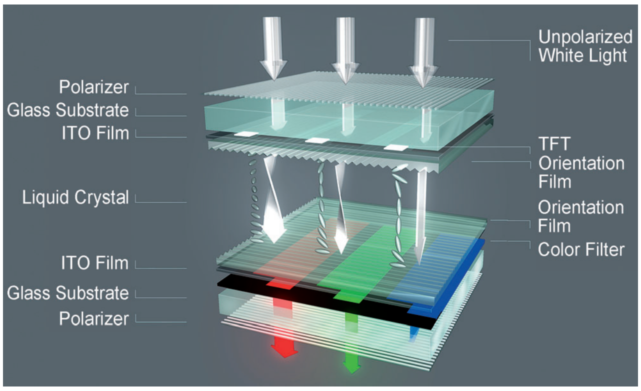
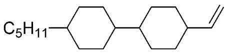
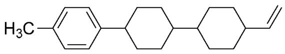
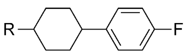
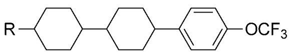
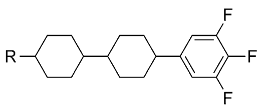


Figure 11. Structure of a TN TFT LCD. The structure of IPS-TFT LCDs and VA-TFT LCDs is explained in *LCD-Explorer* at http://cc-special.merck.de/lcd_explorer/kryptisch.htm (Source: Merck).

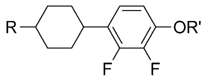
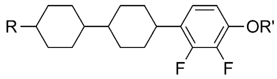
While the STN displays required liquid crystals with special elastic properties such as the alkenylbicyclohexanes **9** or the alkenylphenylbicyclohexanes **10**, the TFT displays needed liquid crystals of outstanding stability and resistivity due to their particular thin film transistor addressing. While the TN and STN displays of the 1980s and 1990s relied on polar cyano-substituted liquid crystals, TFT displays required the use of fluorinated liquid crystals. The fluorinated liquid crystals **11**, **12**, and **13** developed by Merck in 1990 are examples of the next generation of liquid crystals following the cyanobiphenyls **4** and cyanophenylcyclohexanes **5** of the 1970s.[43]

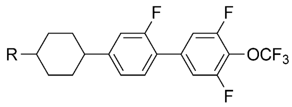
 **9**  **10**

 **11**  **12**

 **13**

As the size of notebook displays increased, all display manufacturers worked not only to improve switching times and lower the driving voltages but also, and above all, to continue to improve the viewing angle dependence of the TN TFT displays, which now were all covered by the Merck VIP patent; the licensing revenue enabled Merck to expand its liquid crystal research within the company even further. Following the success of the LCD notebooks, effort was devoted from the mid-1990s onward to the development of LCD monitors for desktop PCs. Up until then desktop PCs and television sets had been the primary market for CRT screens. In-plane switching (IPS) TFT LCDs were developed by Hitachi[44] and VA TFT LCDs by Fujitsu[45] as LCD technologies offering improved viewing angles. While the ECB and VA modes were already familiar from the 1970s, the IPS mode was invented in 1990 by Günter Baur at the Fraunhofer Institute for Applied Solid State Physics in Freiburg.[46] In the IPS mode the liquid crystals switch in the display plane between comb-shaped electrodes and so provide excellent viewing angle dependence in the IPS TFT LCD. For VA TFT LCDs the liquid crystals with negative dielectric anisotropy were used based on **14** and **15** developed at the end of the 1980s, while for IPS TFT LCDs, in the same way as for TN TFT LCDs, compounds with positive dielectric anisotropy such as **13** or **16** were used.[47] Other devices that were developed with TFT LCDs include LCD projectors, used for direct projection and also in rear projection televisions.

 **14**  **15**

 **16**

The decisive improvement in the switching time of all TFT LCDs came with the introduction of low-viscosity alkenylbicyclohexanes **9**, to which Merck had access through its takeover of the liquid crystals business of Hoffmann-La Roche in 1996.[48] Merck had previously sold its FLC patent portfolio to Hoechst in 1995, as it did not seem possible to derive any commercial benefit from the FLC technology despite faster switching times following the success of the TFT LCDs. In the mid-1990s, the advent of IPS LCDs, VA LCDs, and normal TN TFT LCDs brought on flat screens as alternatives to CRT monitors for desktop PCs and, in less than 10 years, the era of the cathode ray tube was over. Outstanding researchers who received recognition for the breakthroughs in the physics and chemistry of liquid crystals, more than 100 years after their discovery, were Pierre-Gilles de Gennes with the 1991 Nobel Prize in Physics and George W. Gray with the Kyoto Award for Materials Science and Engineering in 1995 (Figure 12).

Factors that contributed to Merck's success in the 1990s were wide-ranging patenting (more than 2000 liquid crystal patents), coupled with a general openness to cross-licensing

Figure 12. Kyoto Award winner, George Gray (1926–2013) (seated, second from the left) together with British friends and colleagues and senior Merck executives (source: Merck).

with the Japanese competition (Chisso), a clear strategy towards a better understanding of display technology through joint ventures with European LCD component manufacturers (Balzers) and display manufacturers (Philips), and the continuous support of project consortia consisting of industrial partners and research institutions supported by the German Federal Ministry of Education and Research.

From the year 2000 onwards, as screen sizes became ever larger, not only were desktop PC CRT monitors replaced but TFT LCD televisions were developed; these mostly featured VA technology but also in part IPS technology. In recognition of the breakthrough they achieved with liquid crystals in VA TFT LCD screens for televisions, three Merck research scientists, Kazuaki Tarumi, Melanie Klasen-Memmer, and Matthias Bremer received the President's Award for Technology and Innovation I 2003 (Figure 13). To date, in the

Figure 13. The President's Award for Technology and Innovation 2003 (German Future Prize) awarded by German President Johannes Rau to Merck researchers (from right to left) Kazuaki Tarumi, Melanie Klasen-Memmer, and Matthias Bremer; on the left Wolf von Lojewski (from the German television network ZDF) (source: Merck).

16 years in which this award has been presented, Merck is the only chemical company to have received it. The triumph of VA TFT LCDs over cathode ray tubes for TV applications then led to a massive increase in demand for liquid crystals with negative dielectric anisotropy which, because of the patent situation, only Merck was allowed to produce for many years.

In order to cover the future needs of TFT LCD manufacturers, now vigorously expanding in Korea and Taiwan also, Merck in 2004, a year in which liquid crystals at Merck celebrated their hundredth birthday, invested 250 million euros in production facilities in Darmstadt. Key to the success achieved in this phase of expansion of the liquid crystal business, with its hundreds of different liquid crystals and thousands of customer-specific liquid crystal mixtures, has been "Operational Excellence"—continuous improvement and sustainable process optimization in a customer-focused business environment.

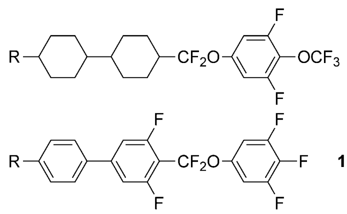
Other key success factors that have made the liquid crystals business so successful have been described by two former chairmen of the Merck Executive Board: Bernhard Scheuble (2004) in his book *The history of the future*[24] and Michael Römer (2009) in the article "Die Welt wird flacher" published in the journal *Chemie in unserer Zeit*.[49] In the last two decades both men have helped co-write the 100-year history of liquid crystals:

"*The considerable success of liquid crystals is the work not of individuals, but of a team. It was necessary to draw a deep breath.*[49]

"Also, our business philosophy contributed to this success: Product development was to take place locally, that is, in direct contact with the customer. This was the motivation for the very early establishment of a research and development center for liquid crystals and their mixtures in Japan, later followed by Korea and Taiwan. At that time, work in this field proceeded with much enthusiasm and the will for great achievement. This continues to this day, always accompanied by a quantum of humor."[24]

For television applications Merck has in recent times used photopolymerizable bisacrylate monomers as special additives for VA technology. The use of these monomers, in polymer-stabilized vertical alignment (PSVA), leads to far superior viewing angles. Although these materials were first developed in the 1990s for LCD compensation films, they achieved their commercial breakthrough only two years ago through their use in 3D LCD TVs and PSVA TFT LCD televisions.

Through the development of materials for TN TFT LCDs and also for IPS TFT LCDs, liquid crystals with positive dielectric anisotropy have been improved further through the introduction of the CF_2O bridge in **17** and **18**.[50]



It was only with the advent of liquid crystal mixtures developed for IPS technology, and in particular its variant, the fringe field switching (FFS) technology, that the breakthrough in tablet PCs was achieved. Thanks to liquid crystals developed at Merck you can read *Angewandte Chemie* on these devices.

How will LCD technology continue to develop? For a number of years now the research departments at Merck have been working intently on fast switching blue phase mode LCDs.[51] These might even work without the need for a color filter through the use of RGB-LEDs, though these displays are presently only at the prototype stage.[52] Owing to the fact that Reinitzer was the first person to witness the blue phase in 1888—Horst Stegemeyer had already mentioned the year of their discovery at the centenary celebration of liquid crystals in 1988[53]—in 2013 we can look back not only on 125 years of *Angewandte Chemie* and 125 years of liquid crystals, but also on 125 years of blue phase.

Now, 125 years after the discovery of liquid crystals, what topics are at the focus of academic research in this area?

Highlighting any (more or less arbitrary) current research topic—especially in the context of this Essay—must of course be well founded. Nevertheless it is right to mention two current examples which are characterized in particular by their exceptionally aesthetic textures under the polarizing microscope.

First, a large variety of smectic phases exist. Smectic phases are closer to the crystalline phase than the technically relevant nematic or cholesteric phase and, in case they have not yet been properly understood and assigned, are systematically numbered for simplicity.[54] Among this series of smectic phases is the so-called B7 phase in banana-shaped (bent-core) liquid crystals the textures of which produce spectacular effects such as spirals or checkerboard patterns (Figure 14).[55]

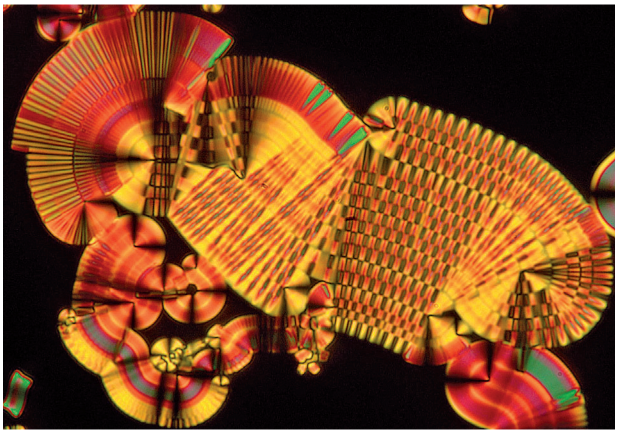


Figure 14. Texture of the smectic B7 phase of a bent-core liquid crystal (with kind permission from Dr. Rajdeep Deb, JRE Group of Institutions, Greater Noida. Ref. [55]).

Then, on the other hand, longer DNA sequences with a chain length of approximately 10 nucleotides exhibit columnar liquid crystal phases in concentrated aqueous solutions, and again display astonishing artistic beauty (Figure 15).[56]

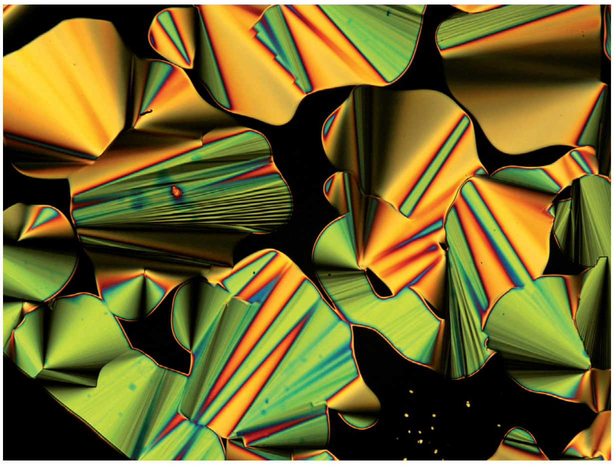


Figure 15. Texture of a columnar phase of short double-stranded DNA helices consisting of 12 nucleotides (CGCGAATTCGCG) in aqueous solution (with kind permission from Dr. Giuliano Zanchetta, University of Milan. Ref. [56]).

Does this research into short-chain DNA helices from laboratories specializing in molecular biophysics and complex fluids somehow hark back to the beliefs of Lehmann and Haeckel of 100 years ago—that liquid crystals are a bridge between nonliving and living matter? We know nowadays, of course, that not only thermotropic but also lyotropic liquid crystals (such as DNA helices) form nematic and cholesteric phases with similar textures.

Even after 125 years, liquid crystals are still fully capable of posing a challenge. Researchers often devote their whole lives to one subject, like Lehmann and Vorländer. Reinitzer, on the other hand, soon turned his attention to other issues as Rector of the University of Graz. Chemistry can often find its own answers, as Ostwald stated in his memorial speech in honor of Robert Bunsen:[57] "*A chemist who is not a physicist is nothing*." And sometimes chemistry, according to George Whitesides,[58] who quotes the science philosopher Thomas Kuhn and his work *The Structure of Scientific Revolutions*,[59] is faced not only with the problems of so-called normal science, but also with scientific revolutions. In the case of liquid crystals, after 30 years of discussion mineralogist Friedel was not only the first to articulate the paradigm according to Kuhn but also to take the first step towards the paradigm shift. And it was finally through physicist de Gennes, whom the Nobel Committee described as "*the Isaac Newton of our age*",[60] and his theory that the paradigm shift was complete. After less than 10 years de Gennes then moved on from liquid crystals to further scientific challenges and also to industry to join the Board of Directors of the specialty chemical company, Rhodia.

6. Outlook for Merck

In the last few decades the chemical company Merck has undertaken continuous pioneering work in the scientific and commercial development of liquid crystals and has built up an extremely successful specialty chemicals business. In order to be successful in the future, too, its philosophy must be not simply to rest on the laurels of past successes but to continue to adapt its business strategies to future challenge. This approach is especially apt in such a dynamic field as the display market. Any successful business is inherently threatened—Merck faces a two-edged Damocles' sword: the one edge takes the form of pursuing competitors, the other presents the possibility of being overtaken by other technologies.

To continue to play a leading role in LCD technology Merck, with its "Displaying Futures" symposium series,[61] is deliberately departing from the path of traditional industrial research and development with its linear technology-centered approach. This initiative is an innovative concept which Merck has called into being to unite experts from various fields (artists, architects, scientists, urban planners), so they can draw up a picture of the future from their own perspectives. The initiative is intended to foster multidisciplinary discussion and deliver inspirational ideas with regard to the future properties, demands, and applications of displays. The emphasis is on new, revolutionary architectural concepts in which various innovative technologies merge with a broad array of display applications and on the question as to what mobility for city dwellers might look like in 20 years and what part displays might play in this vision.

Since the pioneering work of Tang und Van Slyke, who in 1987 were the first researchers (at the Eastman Kodak Company) to realize electroluminescence in low-molecular-weight compounds in diode setups,[62] OLED technology has been seen as an attractive alternative to LCD technology. As one of the leading manufacturers, Merck offers a complete portfolio of materials for OLED displays. These include small molecules for vacuum processing and soluble material systems for printing.

Right now in the present phase of OLED commercialization a significant trend in modern industrial materials research is becoming manifest: the focus is no longer simply on the de novo design of new materials or molecules—increasingly, system innovations and integrated solutions are predominant under the spotlight. Strategic partnerships along the entire value chain in new value-added clusters are increasingly the guarantor of economic success—because it is rarer for single companies alone to manage to establish their crucial technological innovations in the marketplace. With this in mind, at the end of 2012 Merck and Seiko Epson signed a cooperation and licensing agreement for inkjet printing inks for use in the manufacture of displays with organic light emitting diodes (OLEDs). The use of inkjet technology for printing OLED displays requires the marriage of long-life OLED materials and ink technology for the fast and precise printing of the OLED materials. The partnership combines the capability of Merck with regard to high-quality, long-life OLED materials for inkjet production with the expertise of Epson with regard to the technology for converting the OLED materials into printing inks that can be applied using inkjet printing systems.

OLED technology is now successfully established in the smartphone display market and is incorporated in prominent products. Since February 2013 the first 55″ OLED TVs have been available for purchase in Korea. These have so far only been individual success stories as today more than four billion people use liquid crystal displays in their mobile communication devices, and it has been claimed that "*LCD will remain the absolutely dominant technology up until the end of the decade*".[63] 125 years after Reinitzer's discovery, liquid crystals are an excellent example of applied chemistry thanks to their success in display applications.

Received: February 19, 2013
Published online: June 5, 2013

[1] D. Gerlach, *Geschichte der Mikroskopie*, Harri Deutsch, Frankfurt, **2008**.
[2] a) E. Haeckel, *Die Radiolarien*, Georg Reimer, Berlin, **1862**; b) E. Haeckel, *Kunstformen der Natur*, Bibliographisches Institut, Leipzig, **1904**; c) M. Burba, *Mikrokosmos* **2007**, *96*, 7 – 17.
[3] F. Reinitzer, *Monatsh. Chem.* **1886**, *7*, 597 – 608.
[4] F. Reinitzer, *Monatsh. Chem.* **1888**, *9*, 421 – 441.
[5] P. M Knoll, H. Kelker, *Otto Lehmann: Erforscher der flüssigen Kristalle*, **1988**.
[6] O. Lehmann, *Z. Phys. Chem.* **1889**, *4*, 462 – 472.
[7] C. Krauch, *Die Prüfung chemischer Reagentien auf Reinheit*, Brill, Darmstadt, **1888**.
[8] R. Schenck-Marburg, *Z. Elektrochem.* **1905**, *11*, 951 – 955.
[9] *Z. Angew. Chem.* **1906**, *19*, 1637 – 1641.
[10] E. Haeckel, *Kristallseelen*, Alfred Kröner, Leipzig, **1917**, pp. 23 – 38.
[11] D. Vorländer, *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 803 – 810.
[12] C. Mauguin, *Bull. Soc. Fr. Mineral.* **1911**, *34*, 71 – 117.
[13] M. Planck, *Zeitschr. VDI* **1933**, *77*, 185 – 190.
[14] G. Friedel, *Ann. Phys.* **1922**, *18*, 273 – 474.
[15] T. Sluckin, D. Dunmur, H. Stegemeyer, *Crystals that flow*, Taylor & Francis, London, **2004**, pp. 163 – 233.
[16] C. W. Oseen, *Trans. Faraday Soc.* **1933**, *29*, 883 – 900.
[17] D. Vorländer, *Chemische Kristallographie der Flüssigkristalle*, Akademische Verlagsgesellschaft, Leipzig, **1924**, p. 89.
[18] P. Chatelain, *Bull. Soc. Fr. Mineral.* **1944**, *66*, 105 – 130.
[19] G. H. Brown, W. G. Shaw, *Chem. Rev.* **1957**, *57*, 1049 – 1157.
[20] J. Fergason (Westinghouse), US 3,114,836, **1963**.
[21] a) W. Maier, A. Saupe, *Z. Naturforsch. A* **1959**, *14*, 882 – 889; b) W. Maier, A. Saupe, *Z. Naturforsch. A* **1960**, *15*, 287 – 292.
[22] G. H. Heilmeier, L. A. Zanoni, L. A. Barton, *Proc. IEEE* **1968**, *56*, 1162 – 1171.
[23] G. H. Heilmeier, L. A. Zanoni, *Appl. Phys. Lett.* **1968**, *13*, 91 – 93.
[24] Merck KGaA, *The History of the Future—100 Years of Liquid Crystals at Merck*, **2004**.
[25] R. Steinsträßer, L. Pohl, *Angew. Chem.* **1973**, *85*, 706 – 720; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 617 – 630.
[26] H. Kelker, B. Scheurle, *Angew. Chem.* **1969**, *81*, 903 – 904; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 884 – 885.
[27] M. Schadt, W. Helfrich, *Appl. Phys. Lett.* **1971**, *18*, 127 – 128.
[28] M. F. Schiekel, K. Fahrenschon, *Appl. Phys. Lett.* **1971**, *19*, 391 – 393.
[29] G. W. Gray, K. J. Harrison, J. A. Nash, *Electron. Lett.* **1973**, *9*, 130 – 131.
[30] C. H. Gooch, H. A. Tarry, *J. Phys. D* **1975**, *8*, 1575 – 1584.
[31] D. Demus, H. J. Deutscher, F. Kuschel, H. Schubert, DE 24 29 093, **1975**.
[32] a) R. Eidenschink, D. Erdmann, J. Krause, L. Pohl, *Angew. Chem.* **1977**, *89*, 103; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 100; b) R. Eidenschink, D. Erdmann, J. Krause, L. Pohl, *Angew. Chem.* **1978**, *90*, 133; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 133 – 134.
[33] L. Pohl, R. Eidenschink, F. del Pino, G. Weber, (Merck), US 4,398,803, **1983**.
[34] P. G. de Gennes, *Mol. Cryst. Liq. Cryst.* **1971**, *12*, 193 – 214.
[35] R. B. Meyer, L. Liebert, L. Strzelecki, P. Keller, *J. Phys. Lett.* **1975**, *36*, 69 – 71.
[36] N. A. Clark, S. T. Lagerwall, *Appl. Phys. Lett.* **1980**, *36*, 899 – 901.
[37] H. Finkelmann, H. Ringsdorf, J. H. Wendorf, *Makromol. Chem.* **1978**, *179*, 273 – 276.
[38] T. J. Scheffer, J. Nehring, *Appl. Phys. Lett.* **1984**, *45*, 1021 – 1023.
[39] M. Schadt, M. Petrzilka, P. R. Gerber, A. Villiger, *Mol. Cryst. Liq. Cryst.* **1985**, *122*, 241 – 260.
[40] a) V. Reiffenrath, J. Krause, H. J. Plach, G. Weber, *Liq. Cryst.* **1989**, *5*, 159 – 170; b) V. Reiffenrath, J. Krause, A. Wächtler, T. Geelhaar, (Merck), EP 0332024, **1989**; c) T. Geelhaar, *Ferroelectrics* **1988**, *85*, 329 – 349.
[41] T. Nagayasu, M. Hijikigawa, I. Washizuka, *Proc. Int. Display Res. Conf.* **1988**, 56 – 58.
[42] T. Geelhaar, *Liq. Cryst.* **1998**, *24*, 91 – 98.
[43] H. J. Plach, G. Weber, B. Rieger, *Proc. SID* **1990**, 91 – 94.

[44] M. Oh-e, M. Ohta, S. Aratani, K. Kondo, *Asia Display* **1995**, 577 – 580.
[45] K. Ohmuro, S. Kataoka, T. Sasaki, Y. Koike, *SID Dig.* **1997**, 845 – 848.
[46] R. Kiefer, B. Weber, F. Windscheid, G. Baur, *Proc. Jpn. Display* **1992**, 547 – 550.
[47] K. Tarumi, M. Bremer, T. Geelhaar, *Annu. Rev. Mater. Sci.* **1997**, *27*, 423 – 441.
[48] D. Pauluth, T. Geelhaar, *Nachr. Chem. Tech. Lab.* **1997**, *45*, 9 – 15.
[49] M. Römer, W. Becker, *Chem. Unserer Zeit* **2009**, *43*, 94 – 99.
[50] a) P. Kirsch, M. Bremer, *Angew. Chem.* **2000**, *112*, 4384 – 4405; *Angew. Chem. Int. Ed.* **2000**, *39*, 4216 – 4235; b) P. Kirsch, M. Bremer, A. Taugerbeck, T. Wallmichrath, *Angew. Chem.* **2001**, *113*, 1528 – 1532; *Angew. Chem. Int. Ed.* **2001**, *40*, 1480 – 1484.
[51] M. Heckmeier, M. Czanta, A. Goetz, P. Kirsch, L. D. Farrand, A. Taugerbeck, E. Montenegro, (Merck), US 7,440,160, **2003**.
[52] H. Kikuchi, H. Higuchi, Y. Haseba, T. Iwata, *SID Dig.* **2007**, *38*, 1737 – 1740.
[53] H. Stegemeyer, H. Kelker, *Nachr. Chem. Tech. Lab.* **1988**, *36*, 360 – 364.
[54] G. Pelzl, S. Diele, W. Weissflog, *Adv. Mater.* **1999**, *11*, 707 – 724.
[55] R. Deb, R. K. Nath, M. K. Paul, N. V. S. Rao, F. Tuluri, Y. Shen, R. Shao, D. Chen, C. Zhu, I. I. Smalyukh, N. A. Clark, *J. Mater. Chem.* **2010**, *20*, 7332 – 7336.
[56] M. Nakata, G. Zanchetta, B. D. Chapman, C. D. Jones, J. O. Cross, R. Pindak, T. Bellini, N. A. Clark, *Science* **2007**, *318*, 1276 – 1279.
[57] W. Ostwald, Gedenkrede auf Robert Bunsen, *Gesammelte Abhandlungen*, Engelmann, Leipzig, **1904**.
[58] G. M. Whitesides, *Chem. Eng. News* **2007**, *85*, 12 – 25.
[59] T. S. Kuhn, *The Structure of Scientific Revolutions*, *3rd ed.*, University of Chicago Press, Chicago, **1996**.
[60] http://www.nobelprize.org/nobel_prizes/physics/laureates/1991/.
[61] *Displaying futures*, Trademark Publishing, Frankfurt am Main, **2011**.
[62] C. W. Tang, S. A. Van Slyke, *Appl. Phys. Lett.* **1987**, *51*, 913.
[63] K.-L. Kley in *Frankfurter Allgemeine Zeitung*, October 25, 2012.

