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# Part I

## Fundamentals

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# 1

# Liquid crystalline polymers: a brief history

## 1.1 From rigid-rods to main-chain polymers

In March 1888, a young botanist called Friedrich Reinitzer wrote to Otto Lehmann who was professor of physics at Aachen. He described observations, published that year (Reinitzer, 1888), that esters of cholesterol appeared to have two melting points between which the liquid showed iridescent colours and birefringence. It was sensible to consult Lehmann as he had worked for some time in the field of crystal transitions and, above all, had developed a polarising microscope with a hot stage, which was to become a central feature of much of his research. He confirmed Reinitzer's observations, and postal collaboration between the two over the next few years laid the foundations of liquid crystal science. By 1889, Lehmann was describing the material as 'flowing crystals' and the following year as 'crystalline liquids' (Lehmann, 1889, 1890). From this point onwards, he was making most of the running and gradually became the hub of a wider collaboration. He spread interest beyond Germany, notably to France and Holland. Liquid crystal science continued to mature and synthetic chemists, in particular Vorländer at Halle, demonstrated the principles of molecular design which underpin the field. There was considerable debate between George Friedel, working in Strasbourg, and Lehmann and Vorländer, as to the existence of different types of liquid crystalline phase. However, the issue eventually reduced to one of semantics, as it was recognised that liquid crystallinity does indeed appear in several different guises.

The year of Lehmann's death, 1922, marked two important developments. Friedel published a monumental paper (Friedel, 1922) which cleared up much of the terminology of the subject. Drawing on Greek roots he introduced the terms, 'nematic', 'smectic' and also 'mesophase', which he suggested should supplant 'liquid crystals' as the generic title. The second development was within a different scientific community altogether. Staudinger, was mounting his challenge to the chemistry establishment with the notion that long-chain molecules could actually exist. Vorländer seemed rapidly at ease with the idea of polymer molecules, and as early as 1923 he began to pursue the concept of a main-chain liquid crystalline polymer (LCP), systematically studying the effect of increasing the length of liquid crystalline molecules (Vorländer, 1923). He synthesised rods with one, two and three benzene rings *para*-linked through ester groups, and noted their increasing transition temperatures. His discussion of polymers based on these units is illustrated with a note of the

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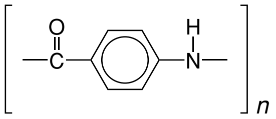


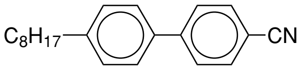
<1>
poly(*p*-benzamide), PBA

synthesis of poly(*p*-benzamide) <1> (see Table 3.3, page 76). He found that the polymer would not melt, reporting it as a birefringent powder which chars without softening. In many respects, Vorländer can justifiably be seen as the father of polymeric liquid crystals. An interesting review of his work has been given by Bruce *et al.* (1997).

While the problem of synthesising polymers which were mouldable in the liquid crystalline phase was only solved finally by Jackson some 50 years later (Jackson and Kufuss, 1976), there was increasing interest in rod-like macromolecules which occurred in nature and formed liquid crystalline phases when in solution (lyotropic phases). A key observation was that of Bawden and Pirie (1937) who noted that solutions of tobacco mosaic virus (TMV) (see, e.g. Sections 3.6.7 and 7.4.4), a stiff rod-like particle a few hundred nanometres long, separated into two liquid phases one of which was birefringent. They also showed that the birefringent phase had a higher concentration of virus. This line of approach continued slowly over the next 20 years or so, other rod-like viruses such as the cucumber virus and the potato virus being added to the list. Bernal and Fankuchen (1941) examined the liquid crystalline phase with X-ray diffraction while Oster (1950) carried out light scattering measurements.

Activity now moved to the laboratories of Courtaulds at Maidenhead in England, where as part of a programme to develop synthetic silk they produced a series of polyglutamates, particularly poly($\gamma$-benzyl-L-glutamate) (PBLG) (see molecule <25> on page 76). These polymers showed liquid crystalline phases in solution and formed the basis of a particularly detailed study of structure and phase equilibria published by Robinson (1956). Although PBLG fibres were spun from the lyotropic phase by Ballard in 1958 they were not developed into a product (Ballard, 1958). The first successful commercialisation of LCPs was achieved by DuPont with their aromatic amide fibre, marketed as Kevlar$^{\mathrm{TM}}$ (molecule <47> on page 92). This fibre, which has outstanding tensile properties, was developed by Kwolek and her team through the 1960s (Kwolek, 1971). It was spun from a lyotropic solution using comparatively fierce solvents such as 100% sulphuric acid which were then washed out from the fibre. While the liquid crystalline nature of the aromatic amide solutions was recognised by those working with them, it is interesting that developments of semi-rigid chain polymers in other areas, such as those involving modified celluloses, proceeded without the realisation that some of their particularly interesting properties were the result of liquid crystallinity.

Vorländer's effort to make a main-chain LCP which would be stable without the addition of solvents was frustrated by the fact that the crystal melting point of rigid-chain crystals increases rapidly with increasing chain length. Research by Jackson and coworkers in the Kingsport laboratories of Eastman Kodak in the 1970s led to the synthesis of rigid, random copolymers of aromatic polyesters. In this way the melting point was much reduced, if



<2>
8CB

not eliminated altogether, and the polymer could be processed as a liquid crystalline melt without risk of degradation. The contribution of Jackson has been seminal to the field. In addition to patents he has published a series of papers, the first of which, with Kufuss (Jackson and Kufuss, 1976), really brought LCPs to the attention of the polymer community at large. Eastman Kodak were also very generous with research samples and within a few years interest in the field had blossomed in industry and academe worldwide.

Main-chain thermotropic LCPs are now firmly established as an important class of material, with most major polymer manufacturers offering their own variations. The inherent high cost of these polymers, coupled with processing difficulties (e.g. they can only be moulded at high temperatures and they are susceptible to weld-line failures unless great care is taken over the design and filling of the mould), means that they are unlikely ever to be produced in large volumes, or to be used for large-scale engineering projects. In fact, most leading LCP manufacturers currently produce between 5000 and 10 000 tonnes per year, which represents a tiny fraction of the total annual global production of polymers. However, mouldable LCPs have found a niche in which their mechanical, thermal and rheological properties are all exploited to the full. The principal uses of Vectra™ (Ticona), Xydar™ (Solvay), Zenite™ (DuPont) and other related materials is in the production of high precision mouldings for use in the electronics industry. Liquid crystal polymers are used for multiway electrical connectors, components in printers and disk drives, transformer bobbins and encapsulation for surface mounted silicon chips, to mention just a few of their applications. They are found in mobile phones, automobiles, computers and many other domestic appliances, so that they can truly be said to have arrived.

## 1.2 The development of side-chain liquid crystalline polymers

Thus far, the development of LCPs since the 1930s has been traced independently from progress in the field of conventional (small molecule) liquid crystals. Research into small molecule liquid crystals went through a relatively quiet period during the 1940s and 1950s. However, the development of liquid crystal displays (LCDs) in the 1960s, produced a veritable explosion of research activity, which often involved chemists and physicists working closely together to develop new molecules, and gain better understanding of their behaviour. The first proposal for an LCD came from Richard Williams, a physical chemist working at RCA's David Sarnoff Research Centre (Williams, 1962), and relied on dynamic light scattering (see Section 8.9). However, the first twisted nematic devices, the true fore-runners of modern displays, did not appear until the beginning of the 1970s (Helfrich and Schadt, 1970; Fergason, 1971), and it was only with the development of a chemically stable range of cyano-biphenyl liquid crystals (e.g. 8CB <2>), by George Gray and Ken Harrison at Hull (Gray *et al.*, 1973), that such devices really became commercially viable. Now that large

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area liquid crystal computer displays containing millions of coloured pixels are routinely produced, it is easy to forget how recently the technology has come of age.

The involvement of polymeric materials in the small molecule field, has been largely a matter of adding active rod-like groups, similar to conventional liquid crystalline molecules, onto flexible polymer chains. They have been added either as side-chains, to form side-chain LCPs, or into the backbone itself, making semi-flexible main-chain materials. The main driving force behind the development of side-chain LCPs was the desire to incorporate them into displays. Side-chain materials offered attractive advantages, both in processing and applications. For example, it was thought it would be possible to produce large-area, flexible displays, forming the side-chain material into films without the need for containment in a cell. Unfortunately, initial results in this field were disappointing, with the liquid crystalline phase of the small molecule being lost on formation of the polymer.

The key advance in the development of side-chain materials was the realisation by Finkelmann, Ringsdorf and coworkers (1978) that rod-like side-chains would only readily form mesophases if they were decoupled from the backbone to which they were attached, by means of a short length of flexible chain acting as a spacer. This discovery led to the synthesis of an extremely rich and varied range of new materials. However, the activity and, in particular, the field orientability of the rigid groups is modified because of their attachment to the chain. In particular, time constants are lengthened, which is a great disadvantage in information displays, although less of an issue for information storage devices. As a consequence, there are, at the time of writing, no commercially available LCDs based on side-chain LCP materials. In fact, small molecule displays continue to be improved at such a rate, that any new technology must offer significant advantages, to convince manufacturers to abandon their investments in existing production lines. Therefore, if side-chain materials are to be exploited in displays they will need to find a niche application, just as main-chain polymers have done, in which their particular properties are an advantage rather than a hindrance.

## 1.3 New trends: networks and elastomers

Interestingly, side-chain LCPs *are* finding uses in displays, but as passive rather than active elements. The unique optical properties of these materials can be very useful in creating thin films with particular birefringence patterns that can greatly enhance the performance of a display (see Section 10.3.4). The materials are often cross-linked, to lock in any particular beneficial arrangement of the molecules. They are often then referred to as liquid crystal networks.

Above their glass transition temperatures, liquid crystal networks become elastomers, and share many of the properties of conventional rubbers. However, on account of their liquid crystalline phases, they also display an intriguing interplay between their mechanical and orientational properties, which leads to many novel applications. Liquid crystal elastomers (LCEs) are relative newcomers to the world of liquid crystals, although their development has been closely connected with that of side-chain materials. They were first postulated by de Gennes (1975) and synthesised by Finkelmann *et al.* (1981). Their potential applications include electromechanical actuators (e.g. artificial muscle) and tunable cholesteric lasers, although none of these have yet been realised commercially. Liquid crystal elastomers continue to provide an active area for research, and offer prospects of exciting new applications in years to come.

## 1.4 Theoretical underpinnings

The gradual development of LCPs, from the early work on TMV in solution to their exploitation as bulk plastic and fibre materials, and most recently as potential electro-optic materials, has been underpinned by advances in theories which explain the detailed observations. Onsager (1949) was the first to introduce a theory of LCPs. By using a virial expansion, he explained the observed biphasic nature of solutions of rigid molecules. A somewhat different approach was that of Flory (1956*a*,*b*) who adapted his lattice model of conventional polymers to the rigid-rod situation. He was able to predict the form of the polymer/solvent phase diagram determined experimentally by Robinson, and his school developed the work over a number of years to the point where it became possible to treat semi-rigid worm-like molecules and also account for specific interchain interactions. The mean-field theory of Maier and Saupe (1959, 1960), originally intended for describing anisotropic interactions between small molecule liquid crystals, was incorporated into the Flory theory, and has been included in many other liquid crystal polymer theories since. In recent years, many new mean-field theories have been developed for polymer liquid crystals, and these are exemplified by the work of Wang and Warner (1987, 1992), who have been successful in predicting the phase behaviour of heterogeneous systems, such as main-chain polymers with alternating rigid and flexible units, as well as side-chain LCPs. This latter work includes the prediction that side-chain polymers can exist in three different nematic mesophases, $N_I$, $N_{II}$ and $N_{III}$, differing in the relative arrangements of the side-groups with the backbone. The key advance in the understanding of LCEs, came with the theory of Warner, Gelling and Vilgis (1988), which relates the mechanical properties of the elastomer to microscopic molecular parameters.

## 1.5 A bright future for liquid crystalline polymers

Main-chain LCPs have already become established as useful structural materials, whose particular properties make them ideally suited to high precision mouldings, as well as for high performance fibres. There seems to be an ever increasing catalogue of products in which they are used, and the current drive towards miniaturisation will ensure even more applications, as conventional polymers fail to possess sufficient stiffness for many small parts. However, it would be wrong to suggest that all applications of main-chain materials are mechanical. One particularly exciting new area is that of light-emitting polymers.

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Many electroluminescent polymers (e.g. the polyfluorenes) are, in fact, liquid crystalline, and this property can be used to advantage during processing to produce oriented systems with polarised emission. The potential market for such a material as a polarised backlight for small-molecule LCDs is enormous. On the other hand, side-chain materials are beginning to show their utility in other ways, as *self-assembled* structures with bespoke optical properties.

It is clear that 'self-assembly', where molecules are designed so that they organise themselves into larger scale structures in order to achieve special properties, will be a significant objective in materials science in the twenty-first century. The demands of nanotechnology require an ever finer control over the molecular arrangements within new materials. The fact that liquid crystallinity itself is a form of orientational self-assembly, coupled with the fact that the molecules in a mesophase can be steered by external fields, means that the principles underlying the science of LCPs can only grow in significance in the years ahead.

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