

Metallomesogens

Synthesis, Properties,
and Applications

Edited by José Luis Serrano



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Metallomesogens

Synthesis, Properties,
and Applications

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To our families, for the time we neglected them, and especially to Pablo, whose loss saddened us all, and to Manuel, whose arrival restored our happiness.

Biography



José Luis Serrano studied chemistry at the University of Zaragoza, Spain, where he received his Diploma and Ph. D. for work in the field of liquid crystals in the group of Professor Enrique Meléndez. In 1985 he obtained the position of professor titular of organic chemistry at the University of Zaragoza. Since 1985 he has been at the Institute of Materials Science of Aragón (ICMA) and was Vice-Director of the institute from 1987 to 1991. His research interests include ferroelectric liquid crystals and metallomesogens of both low and high molecular weight.

Preface

Some years ago, after attending a lecture on the structural variants of organic mesogens, a Spanish physicist described the field of liquid crystals as being similar to a “treatise on entomology”. Indeed, the review article by Dietrich Demus [1], written on the occasion of the centenary of liquid crystal chemistry, supports this observation, since terms such as “discotic skeleton”, “calamitic”, “phasmidic”, “spinal” and “the anatomy of the liquid crystal” are frequently used. Most of the compounds described in this paper consist of a relatively small selection of elements, such as carbon, oxygen, nitrogen, phosphorus and sulfur together with the halogens. And yet, although their coordination possibilities are somewhat limited, an enormous number of liquid crystalline compounds has been reported [2, 3].

However, just when the number of new syntheses of new structures seemed likely to be exhausted, a new class of compounds with remarkable potential has emerged in recent years: metal-containing liquid crystals or “metallomesogens”. These materials open the door to a rich variety of new geometrical shapes including square-planar, octahedral, square-pyramidal, sandwich and lantern structures which are, in many cases, unobtainable in purely organic compounds. Thus, a new generation of molecular shapes has appeared, as exemplified by open-book-shaped [4], brick-like [5], shish-kebab-like [6] and worm-like [7] compounds, as well as by a large number of compounds whose shapes are reminiscent of capital letters of the Latin alphabet; for example C, D, H, I, K, O, P, T, U, V, X, and Z.

The field of liquid crystals, as are all areas of materials science, is multidisciplinary. Chemists, physicists and engineers all have an interest in mesomorphic compounds, and frequently their priorities tend not to overlap. In general, the synthesis of new liquid crystalline materials and the study of their structure–property relationship has been the main objective of chemists. In contrast, physicists tend to have quite different interests. Unlike chemists, physicists are not interested in the properties of a series of compounds, but instead prefer to study a sample of a single compound which is both stable and of potential value. This discrepancy between the requirements of chemists and physicists has also affected the field of metallomeso-

gens and, in consequence, an abundance of new materials has been synthesized, but the characterization of their physical properties has lagged far behind. This is probably the most important problem in metallomesogen research. Only by placing a greater emphasis on the physical characterization of these materials will we be able to talk about the real possibilities of these compounds rather than just their potential. Liquid crystal research in general must face this problem. Although thousands of mesogens have been reported, physical properties have been measured of only hundreds of compounds and fewer than a hundred materials have found applications in technical devices.

In contrast, far fewer metallomesogens have been synthesized and yet, although this field is still in its infancy, considerable advances in the understanding of their physical properties have been made, as highlighted by the following reports on:

- Novel types of ionic thermotropic liquid crystals [8] and covalent soaps [9] of silver derivatives.
- Self-assembling mesomorphic coordination complexes [10, 11].
- One-dimensional conducting metallomesogens [12].
- New liquid crystals showing ferroelectric behavior: square pyramidal oxovanadium complexes showing a unidimensional arrangement possessing supramolecular domains of polarization [13]. Molecules with a chiral mesogenic core [14] and nondiscotic compounds bearing multiple chiral tails [15].
- Paramagnetic liquid crystals showing parallel or perpendicular orientation in magnetic fields [16].
- Induction of mesophases by means of charge-transfer complexation [17].
- Improvement in the processing of high performance aromatic liquid crystal polymers by metal complexation [18].

To date, several reviews have been published on lyotropic and thermotropic low molecular weight metallomesogens [19] and more specifically on calamitic [20], discotic [21] and polymeric metallomesogenic materials [22]. These reviews, on the whole, tend to give a descriptive appraisal of the structure–property relationships in metallomesogens. In this book, we wish to present a general overview of metallomesogens up to the first half of 1994, which will be helpful to all people working in the field as well as to those who have a general interest in this subject. Thus, we have chosen to describe four different aspects of these compounds, namely materials, synthesis, structural characterization methods, and physical properties. Although the subject of metallomesogens is a specialized area of liquid crystals, we have tried to present the material in a self-explanatory way. We have therefore included a general background on the basic concepts of liquid crystals with particular emphasis on mesophase nomenclature and phase classification. In each chapter we have also given a brief explanation of the more significant points discussed. The layout of the book is as follows:

Chapter 1 presents a short introduction to liquid crystals and, in particular, to metallomesogens. Chapters 2–5 focus on metallomesogens with an emphasis on

liquid crystal structure–property relationships. Chapters 6 and 7 outline the synthetic approaches to the preparation of metallomesogens. Chapters 8 and 9 mainly describe the structural characterization methods which are particularly important in the field of metallomesogens: electron paramagnetic resonance (EPR) and diffraction techniques. Other methods, such as polarizing optical microscopy, differential scanning calorimetry (DSC), infrared, and NMR spectroscopy, are commonly used for the study of liquid crystals in general. Chapters 10 and 11 highlight the physical properties of metal-containing compounds. Chapter 10 is devoted exclusively to magnetic properties and reflects the considerable amount of research interest in this subject. All other physical properties studied so far are presented in Chapter 11. Finally, Chapter 12 considers the more fundamental aspects of metallomesogens and attempts to predict future developments in this field.

The authors all belong to the Materials Science Institute of Aragón (ICMA). This research center unites research workers from two different institutions, the University of Zaragoza and the Consejo Superior de Investigaciones Científicas (CSIC). Since its creation in 1985, one of the lines of research at the ICMA has been devoted to liquid crystals. The three main areas of investigation are metallomesogens, ferroelectric liquid crystals and liquid crystalline polymers. All of the authors are involved in one or more of these areas.

A number of people assisted in the preparation of this book. The authors would like to thank Dr. D. Broer, Prof. Dr. V. Orera and Prof. Dr. A.M. Levelut for their meticulous and painstaking revision of some of the chapters in this book. We are indebted to Dr. N. Thompson for his excellent correction of the manuscript (style and in some cases contents). We would also like to thank the rest of the people of the Zaragoza Liquid Crystals Group who have tolerated our hysterical moments and forgave us for devoting less of our time to them. Finally we are grateful to the various editors and workers of VCH (especially Dr. P. Gregory, Dr. U. Anton) for their kind guidance and patience throughout the preparation of this book.

Zaragoza, August 1995

J.L. Serrano

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1 Introduction

José Luis Serrano

1.1 General Concepts: Metallomesogens

The study of metallomesogens, the colloquial and accepted name for metal-containing liquid crystals, is a relatively new area in the field of liquid crystals.

If we do not consider the papers related to alkali and alkaline earth metal soaps, only a few papers dealing with this subject have been published in the literature up to 1986. However, since then a significant increase in the number of reports has occurred (Fig. 1-1).

The field of metallomesogens is considered to be a young branch of the one hundred-year-old liquid crystal science. However, the first account of these materials is as

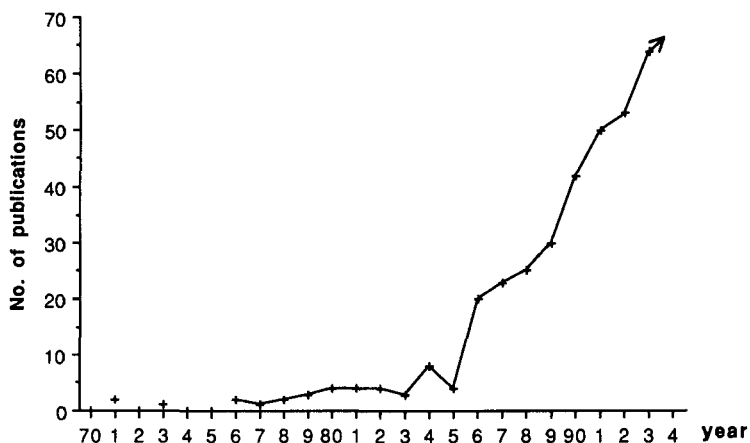


Figure 1-1. Publications on Metallomesogens (excluding alkali and alkaline-earth soaps).

old as the history of mesogenic compounds itself. In the middle of the 19th century, a number of soaps, such as the ones mentioned above, were reported to exhibit double refraction phenomena in aqueous solution [1]. Several of these soaps are alkali metal salts of naturally occurring fatty acids, and they behave as lyotropic metallomesogens. It should be noted that these studies were undertaken forty years before Reinitzer's work on cholesterol derivatives which showed "double melting points" and interesting "color effects". Reinitzer's paper is accepted to be the earliest manuscript on liquid crystals [2]. Later, he also reported on the appearance of similar phenomena for the silver salt of cholesteric acid [3]. This could be the first reference to a liquid crystal containing a transition metal. However, it is broadly accepted that the first paper dealing with metallomesogens appeared in 1910. Vorländer described the thermotropic properties of alkali metal carboxylates which, in some cases, exhibit lamellar phases upon melting [4]. Once again the soaps!

During the next three decades a number of authors [5] further studied the phases observed in soap solutions. However, as far as metallomesogens are concerned, it was not until 1960 that this field of research was significantly stimulated, mainly by Skoulios and Luzzati [6]. In fact, amphiphilic compounds were studied from the basis of a sub-discipline in its own right, which a large number of metallomesogens belongs [7].

In contrast, only one paper dealing with covalent metallomesogens was published in the same period of time. Once again, it was Vorländer who described the smectic arrangement in some diaryl mercury Schiff base derivatives in 1923 (Fig. 1-2a) [8]. In 1957 Graham et al. reported a liquid crystal phase in ferrocenecarboxaldehyde, but

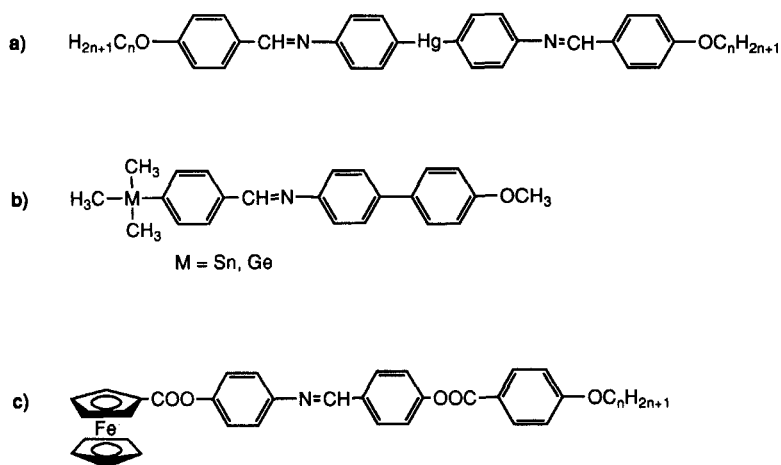


Figure 1-2.

later studies carried out by Verbit et al. proved that this phase is in fact a plastic crystal [9]. Until the 1970s no more covalent metallomesogens were described.

In 1971 Young et al. [10] published an often neglected paper, describing the mesogenic properties of several compounds containing group IV elements. In this work, the authors describe the mesomorphism behavior of two Schiff base derivatives of tin and germanium which show two unidentified smectic phases (Fig. 1-2b). These results had previously been presented at the *Third International Liquid Crystal Conference* in Berlin one year earlier.

In 1976 Malthête et al. reported smectic order for a number of ferrocene derivatives (Fig. 1-2c) [11].

As can be seen in Fig. 1-2, the first three covalent metallomesogens described were curiously all organometallic Schiff base derivatives.

The first report on covalent liquid crystalline coordination complexes appeared in 1977. Giroud et al. described the mesomorphic properties of several nickel and palladium dithiolene derivatives (Fig. 1-3) [12].

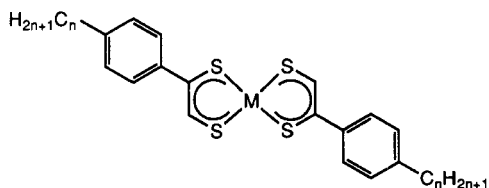


Figure 1-3.

Later, papers describing metallomesogens were sporadically published every year until the “explosion” in metallomesogen research started in 1986. This marked increase in research on metallomesogens gives rise to an important question: Why this sudden interest in these materials?

An overview of the publications concerning metal-containing liquid crystals reveals that the majority of authors, using quite similar words, enclose in their texts an attractive and promising leitmotif: “. . . liquid crystalline materials in which a metal atom is incorporated into the molecular skeleton are of interest because such new materials are expected to have not only the intrinsic properties of organic mesogens but also the unique properties based on metal atoms. . .”.

The possibility of combining the properties of liquid crystals (fluidity, ease of processability, one- or two-dimensional order, etc.) with the properties associated with metal atoms (color, paramagnetism, a electron-rich environment, etc.) is probably the main origin of the progress in this field.

Metallomesogens are certainly a singular example of symbiosis in materials science. Compounds showing interesting magnetic [13] (paramagnetic liquid crystals, control of the molecular orientation in a magnetic field), electrical [14] (one-dimensional conductors), optical [15] (strong birefringence, dichroism, nonlinear optical behaviour) and electro-optical [16] (photoelectric behavior, ferroelectric electro-optic responses) properties have already been obtained.

Likewise, for those fascinated by “chemical architecture” and the relationship between the molecular structure and the physical properties of compounds, the study of metallomesogens has opened up remarkable possibilities to achieve not just new, but unprecedented and more easily accessible liquid crystalline molecular structures than the ones provided by classical organic molecules.

In addition, and perhaps more interestingly, the possibility of tuning the physical (mesomorphic, electrical, optical, magnetic, etc.) properties of metallomesogens is significantly extended, since both the organic ligand and the metal center can be varied. A particular ligand can be complexed to numerous different metal atoms which differ in nature or oxidation state. Alternatively, the well-documented effects of structural modifications found for organic liquid crystals can also be applied to the organic ligand in a coordination complex.

Some of the more important results in these areas of research have already been mentioned in the preface, but many others will be highlighted in the following chapters.

1.2 General Concepts: Liquid Crystals

As explained in the preface, our intention was to write a self-contained book. For this reason we have included the following section which is devoted to the relevant basic concepts in liquid crystals science. For those who wish to gain a deeper insight into this field, a number of excellent books and monographs exist which cover the general topic [17] or more specific areas [18].

In the field of liquid crystals, molecular structure and molecular order play a fundamental role and, although the terminology which has evolved is derived from a number of sources, classical Greek has provided the basis for the terms used (e.g. mesophase, calamitic, smectic, enantiotropic, lyotropic, thermotropic). As a consequence, many researchers not directly involved in this field may find the jargon somewhat intimidating. However, it is sufficient to familiarize oneself with a few relatively simple terms in order to fully understand the general principles which apply to liquid crystals.

Liquid crystals (or mesogens) are materials which exhibit liquid crystalline behavior (or mesomorphism). This behavior appears under given conditions, when phases occur in which the molecular order is intermediate between that of an ordered solid crystal and a disordered liquid or solution; these intermediate phases are called *mesophases*. Liquid crystals have been defined as “orientationally ordered” liquids or “positionally disordered” crystals [19] and combine properties of both the crystalline state (e.g. optical and electrical anisotropy) and the liquid state (molecular mobility and fluidity). There are two different ways in which a mesophase can be formed, and these give rise to the main classes of liquid crystals:

a) Mesophases can be formed by pure compounds (or mixtures of compounds) by the influence of temperature. In this case, the liquid crystal is termed *thermotropic*.

When the thermotropic mesophase appears both in the heating and the cooling process (i.e. when it is thermodynamically stable) it is called *enantiotropic*. Thermodynamically unstable mesophases, which only appear in the cooling process due to the hysteresis in the crystallization point, are referred to as *monotropic*.

b) Mesophases can also be observed as a result of certain species (e.g. amphiphiles) forming anisotropic aggregates in the presence of a solvent (usually water). These mixtures are known as *lyotropic* liquid crystals. The occurrence of a particular lyotropic mesophase depends on the temperature and the constitution of the mixture.

A large number of compounds of both low and high molecular weight (polymers) have been described as thermotropic or lyotropic liquid crystals, and some of them exhibit both types of behavior (*amphotropic* liquid crystals). Thermotropic liquid crystals have gained a relevant place in the field of materials science, whereas lyotropic liquid crystals are of fundamental interest in life science. Both kinds of self-organizing systems play an important role in supramolecular chemistry [20].

The intermolecular forces responsible for the molecular arrangement in liquid crystals are essentially the same as those predominant in molecular solids. However, only molecules containing certain structural elements exhibit liquid crystalline behavior. Mesogenic molecules need to meet a series of structural and electronic criteria [21] so that a satisfactory packing of molecules is achieved which allows appropriate interactions between neighboring molecules. The existence of a permanent dipole moment, its magnitude, or the anisotropy of the molecular polarizability can be determining factors in the promotion of liquid crystallinity.

Thermotropic liquid crystals are classically divided into two main groups depending on their structural features; calamitic (rod-like) (Fig. 1-4a) and discotic (disc-like)

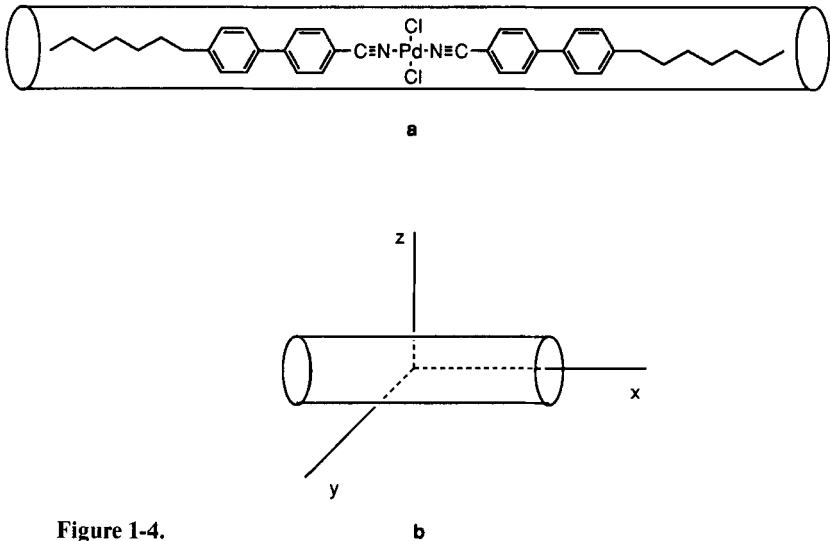


Figure 1-4.

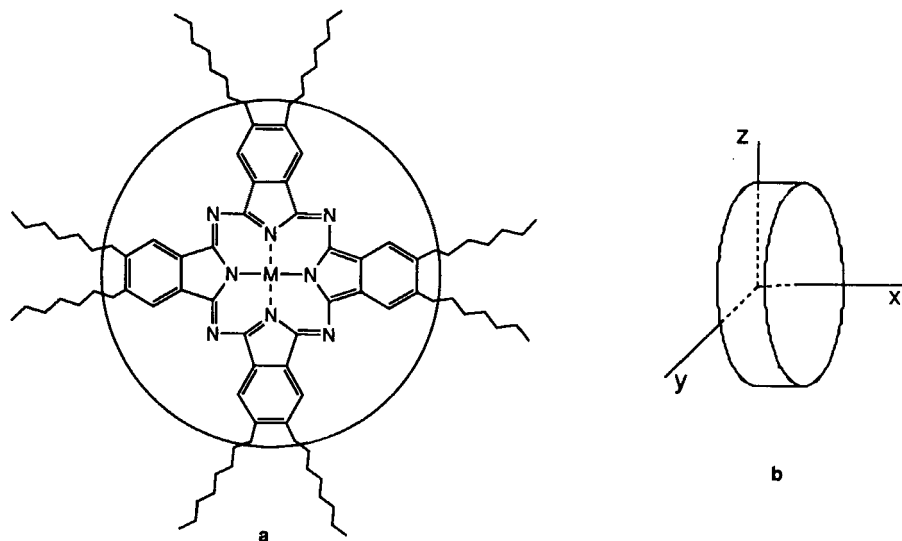


Figure 1-5.

(Fig. 1-5a). In both cases, the molecules can be described as cylinders with a high degree of structural anisotropy. Calamitic compounds have a structure in which the axial component is larger than the radial components (Fig. 1-4b). On the other hand, discotic compounds, as the name implies, are disc-like, therefore the radial components are larger than the axial component (Fig. 1-5 b). Using these theoretical models, the phase transitions shown by a large number of both low and high molecular weight mesogens have been successfully explained. In recent years however, an increasing number of new mesogenic compounds which cannot be described by either model has been reported, including molecules combining both calamitic and discotic shapes (phasmidic compounds), calamitic and discotic twins and compounds with very large lateral substituents. New theoretical models have been proposed in order to explain the mesogenic behavior of these materials [22], for example, a brick-like (sanidic) geometry can be proposed for some cases (Fig. 1-6).

In a similar way, lyotropic liquid crystals [23] can be described by a relatively simple model. In compounds which form lyotropic mesophases, the molecules usually possess the amphiphilic character typical of compounds with surface active properties, and consist of a polar head group and one or more apolar, aliphatic chains. The polar head group can be formed by either ionic moiety (cationic, anionic, or zwitterionic) or by one or more nonionic groups which have strong dipole moments capable of interaction with polar solvents. A representative example is sodium stearate (a soap), which forms a lyotropic mesophase in aqueous solutions (Fig. 1-7).

As in the field of thermotropic liquid crystals, a significant number of lyotropic structures which differ from this typical model have been discovered in recent years.

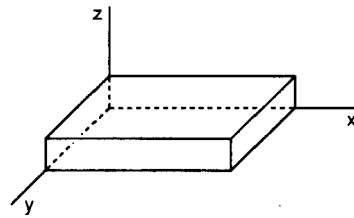
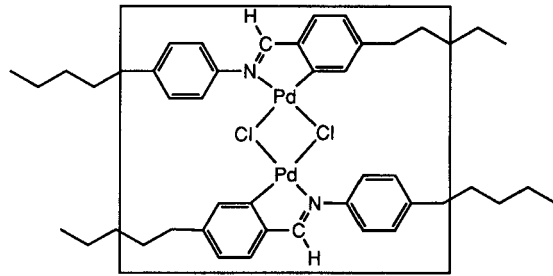


Figure 1-6.

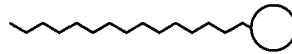
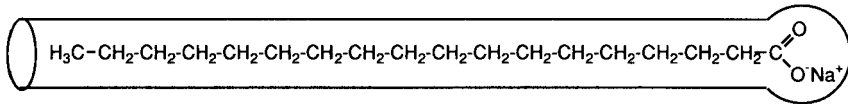


Figure 1-7.

For example, chromonic lyotropic disc-shaped or lath-shaped molecules which, by means of π -interactions, self-organize into columnar mesophases in the presence of a solvent. Most of these molecules do not even incorporate the polar groups which are present in amphiphiles with the more conventional soap structure [24] (Fig. 1-8, see p. 14). Despite these recent departures from convention, the vast majority of thermotropic mesogens described are covalent materials, whereas many lyotropic liquid crystals are ionic.

The preceding discussion refers to low molecular weight compounds, but the conclusions regarding the structure–property relationship, which arose from the systematic investigation of organic liquid crystals molecules can also be applied to macromolecules. Thus, a wide variety of liquid crystalline polymers (LCPs) has been reported. Some of them are commercially available due to their technological advantages with respect to thermoplastic materials for engineering applications. The molecu-

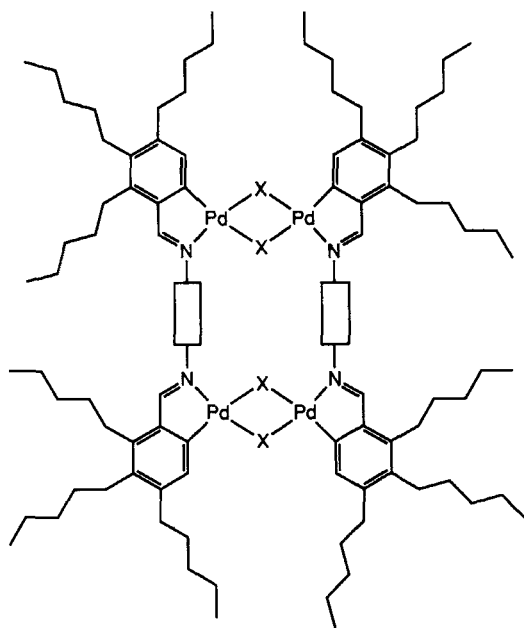


Figure 1-8.

lar architecture of liquid crystalline macromolecules basically depends on the way in which the mesogenic units (either calamitic or discotic) are incorporated into the polymeric chain. The most important types of liquid crystalline polymers are shown schematically in Fig. 1-9. As regards the polymer structure, an initial classification can be established between one-dimensional and crosslinked polymers. The one-dimensional polymers can be classified according to the way in which mesogenic units are introduced into the polymeric backbone. Hence, the two principal types are main-chain LCPs (where mesogenic units are introduced as constituents of the polymer chains) and side-chain LCPs (where mesogenic units are introduced as branches of the polymeric chains). Clearly, there are numerous possibilities for the design of these types of polymers depending on the kind of mesogenic unit introduced. Polymers can be lyotropic or thermotropic, calamitic or discotic or, alternatively, intermediate types (combined LCP) of polymeric structure in which mesogenic units are present both in the main backbone and as side-chains.

The possibility of crosslinking polymer chains further increases the number of polymeric liquid crystalline systems accessible. Thus, liquid crystalline elastomers (materials with a low degree of crosslinking) or anisotropic networks (materials with a high degree of crosslinking) are the latest contributions in this field.

As a consequence of the ever increasing scope of the study of liquid crystals it is becoming increasingly difficult to make a simple classification of mesomorphic materials. Molecular structures which cannot be described by the proposed models are reported more and more frequently. One important contribution to this phenomenon