## Liquid Crystals

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# Topics in the evolution of liquid crystal polymers

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# Plenary Lecture

## Topics in the evolution of liquid crystal polymers

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The relevance of scientific and technical research on liquid crystal polymers is examined and compared to the overall evolution of the general field of liquid crystals. It is shown that polymers have played a progressively increasing role during the last 25 years, and although they only became a quantitatively significant subject not much more than 10 years ago, their contribution to problems and materials now represents a considerable share. Three specific topics concerning rigid rod polymers, liquid crystalline networks and polymeric metallo-mesogens are examined and some related problems highlighted. In particular, some examples showing tractable thermotropic mesomorphic systems can be obtained with linear rigid homopolymers are examined; the phase behaviour of networks derived from segmented chain mesogenic polymers is discussed; inclusion of metallo-organic groups into polymeric mesogens is reviewed.

### 1. Introduction

Reviewing in a single lecture the entire field of liquid crystal polymers (LCPs), even in a cursory way, would be indeed an impossible task on account of the extent and variety of subjects characterizing the research developed in this area. Therefore, I will restrict my attention to some problems concerning three specific subjects chosen out of those we have been interested in during the last few years. However, I believe that, before doing that, it may be worthwhile taking a glance at some comprehensive data on the scientific output concerning LCPs.

Let me start by recalling that while liquid crystallinity has been under discussion for a little more than one century, liquid crystal polymers became a quantitatively relevant subject of experimental research less than 20 years ago. They are younger than the first basic theoretical approaches to liquid crystallinity developed by Onsager, Flory, and Meier and Saupe.

To get an idea of how and how much the field has moved, it may be sufficient to consider even a rough picture (see figure 1) of the scientific output of the last quarter of a century, taking as a reference unit the average output per year of the 1967–71 quinquennium. The comprehensive scientific literature on liquid crystals shows an almost linear increase, but the fraction concerning polymers follows a different trend. It is only 2·5 per cent of the total around 1970; there is then a small relative increase during the following five years, but during 1981 it rises to little less than 10 per cent, to jump close to a 35 per cent share during last year. In different terms, the 1991 scientific output on LCPs, corresponding to $\sim$ 1050 articles or books or patents, is 7·7 times that of 1981 and 47·4 times larger than the output of the entire 1967–71 period.

Since a good share of the interest in LCPs involves practical applications, patenting follows a similar trend. During the years 1972–76, when patenting concerning the use of low molar mass liquid crystals for electro-optical devices boosts strongly, patents concerning polymers are very few, though very important, and the scientific literature

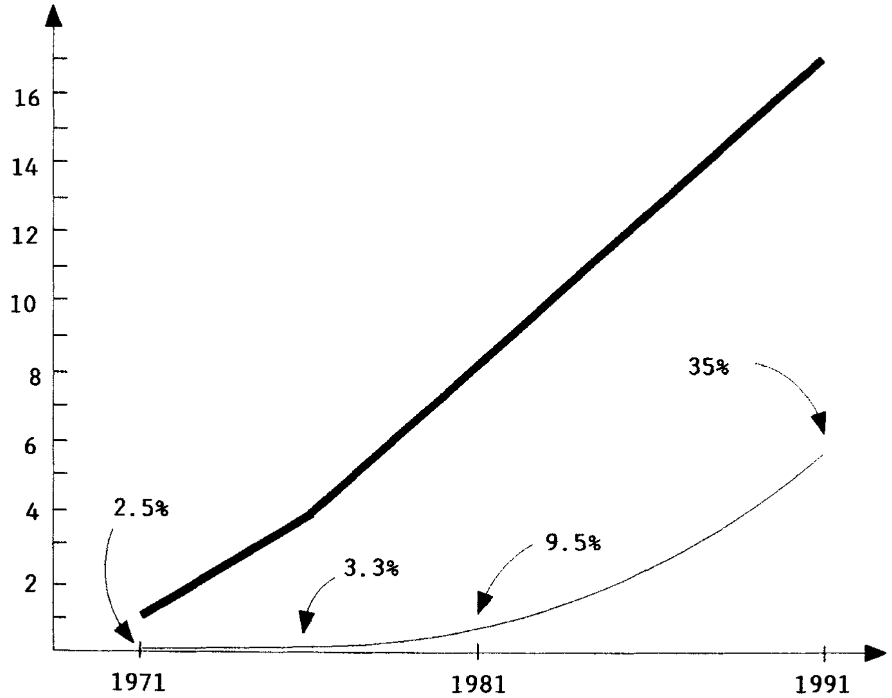

Figure 1. Scientific output (articles and patents) on liquid crystals. Comprehensive data: broad line; polymers: thin line. Average over 1967–71 taken as unity. Elaborated from Chemical Abstracts.

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**Practical uses of LCPs (%) 1991**

*Heat resistant, high strength manufacturables (75 per cent)*
heat resistant, electrical insulators, printed circuits boards
compounds for machine fabrics and electronics parts
laminates with gas barrier properties for packaging films
coatings for optical fibre cores, with good bending strength
mouldings and fibres with high mechanical performances

*Electro- and electro-optical applications (13 per cent)*
rewritable electro-optical recording
electro-conductive films
molecularly oriented resins with good optical properties

*Other applications*
adhesive films for bonding metal sheets
compounds with fluoropolymers for lubricating materials
blends for materials with good metallization properties

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Figure 2. Subjects from the 1991 patent literature on liquid crystal polymers. Elaborated from Chemical Abstracts.

concerning patents is about 5 per cent of the total on LCPs. During 1991 this ratio rose to 22 per cent.

The quantitative increase of interest in LCPs corresponds to a parallel diversification of the scientific and practical goals and has led to a multiplication of the chemical species produced.

It may be interesting to recall that 9 out of 22 articles on liquid crystal polymers, reviewed by Chemical Abstracts in 1967–71, concern poly($\gamma$-benzyl-L-glutamate) and 8 more articles deal with comb-like acrylate polymers. None of these was included in any patenting.

A large number of new LCPs has been synthesized since then, and the variety of practical objectives may be grasped by inspecting the patent literature relating to 1991 (see figure 2).

The number of patents concerning materials with high strength at high temperatures is close to 80 per cent of the total. Many of these materials, notably those intended for use in the electronics industry, are not designed to be used in extreme conditions, but have none the less to meet special requirements concerning, at the same time, mechanical strength, chemical resistance, dielectric properties, and thermal expansion coefficient.

A comparatively small number of patents concern materials designed for optoelectronic applications, for the manufacture of coating or packaging materials with gas barrier properties or even as components of ovenware.

## 2. Thermotropic rod-like homopolymers

Although the quantitative relevance of the patent literature may not necessarily be completely representative of the actual evolution of a scientific field, there is no doubt that the large prevalence of applications relating to structural materials does correspond to a still remarkable scientific interest in that field. Therefore, in switching attention now to specific topics, I think it may be worthwhile to dwell just a little bit on that subject. After that, I will draw attention to two very different subjects: LC networks and polymeric metallo-mesogens.

Scientifically, the field of high strength, high temperature LCPs has grown to a rather inhomogeneous maturity. In fact, while a complete understanding of their rheological behaviour is yet to be achieved and polymer processing may still be a problem, the basic ideas about how to make them are sufficiently well established. Many structural variations of the rod-like theme have been developed with the purpose of either lowering the melting temperature to make polymers thermally processable or increasing the solubility in non-degradative, low cost solvents for solution processable materials.

Particularly for thermotropic polymers, a real breakthrough may be expected only if either new monomers or new synthetic routes to conventional monomers are able to lead to low cost materials.

The large majority of the thermally processable high strength LCPs are random copolymers. This feature, which offers the opportunity of lowering the melting temperature and the additional advantage of allowing a large variability of the polymer properties, has unfavourable effects on their crystallizability and to some extent on the final mechanical properties. Therefore, the quest for new structures includes finding new mesogenic materials that are polymerizable or copolymerizable to thermally processable homopolymers. One way possibly to do that is to increase the wavyness of the polymer chain by use of monomers whose terminal bond directions are not parallel to each other. This is not an entirely trivial problem. Actually, non-linear molecular groups are commonly being used in the production of commercial high modulus LCPs as comonomers intended for interrupting the linearity and the rigidity of the polymer chain. However their non-mesogenic character would make them useless for the formation of homopolymeric LCPs.

Recently, Kricheldorf and Hüner [1] have shown a rather simple way to obtain fully aromatic, melt processable, homopolymeric LCPs utilizing non-linear monomers (see figure 3).

The key structure is a diphenol obtained from 4-hydroxyphthalic acid and 4-aminophenol. It has proved to be a good mesogenic unit for the preparation of liquid crystalline semi-flexible and fully aromatic poly(ester-imides).

A similar example has been developed at Naples University [2].

The polymer is the terephthalic ester of 2-(4-hydroxyphenyl)-6-hydroxybenzoxazole (see figure 4). The synthetic route to the polymer is shown in figure 5. The relevant features of the synthesis of the key compound are outlined in figure 6.

The polymer melts to a liquid crystalline phase, very likely nematic. The degree of crystallinity of the polymer as prepared is about 44 per cent. It decreases to ~33 per cent by non-isothermal (20°C min$^{-1}$ cooling rate) melt crystallization, but may be increased up to 60 per cent by short annealing at temperatures close to incipient melting. Dynamic mechanical analysis shows that a glass transition takes place at 181°C. Isotropization starts at ~470°C, but the temperature cannot be properly defined because chemical decomposition takes place above ~500°C when isotropization is not complete.

Highly oriented semi-crystalline fibres may be obtained by melt spinning. The identity period along the fibre axis, as measured by X-ray diffraction (36·1 Å), corresponds to the sequence of two monomeric units in a polymer chain in the extended conformation. The molecular geometry of this polymer is very close to that of Kricheldorf's poly(esterimide) shown before. Both are affected by regio-irregularity as a consequence of the asymmetry of the diphenolic monomer. However, while the benzoxazole-containing polymer may be crystallized to a considerable extent, the poly(esterimide) shows very poor crystallinity. The reason for this could be connected with the disorder that the constitutional irregularity imposes upon the sequence of polar carbonyl groups.

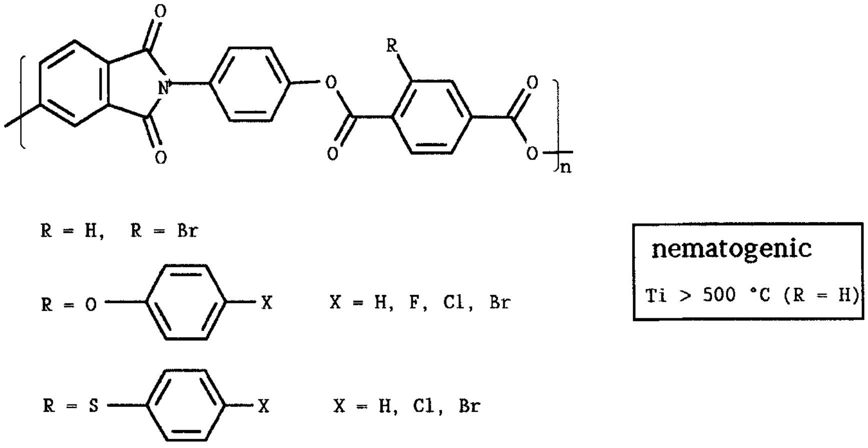
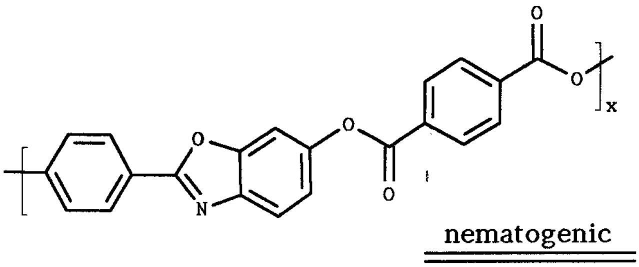


Figure 3. Examples of polyaromatic non-linear LCPs [1].



Tm = 408 °C (44% cryst.)

Tm = 418 °C (61% cryst.) [annealed]

Ti > 500 °C

Figure 4. A 2-phenylbenzoxazole-based non-linear polyaromatic mesogen [2].

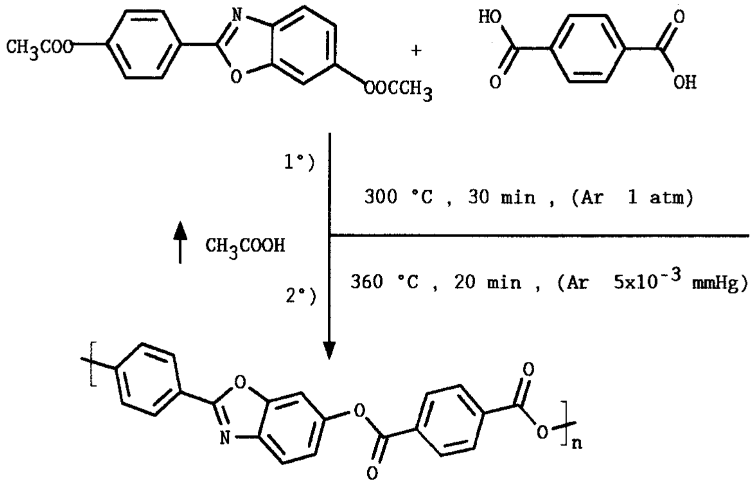


Figure 5. Sketch of the polymerization reaction [2].

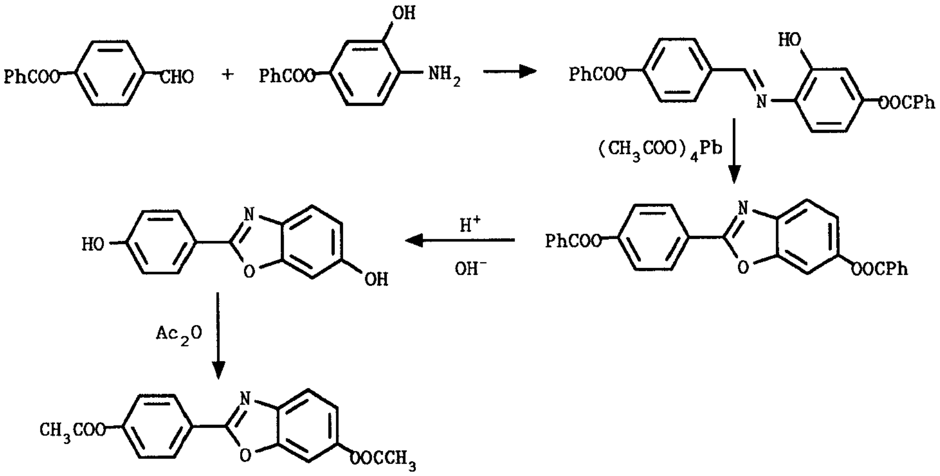


Figure 6. Chemical route to the relevant monomer [2].

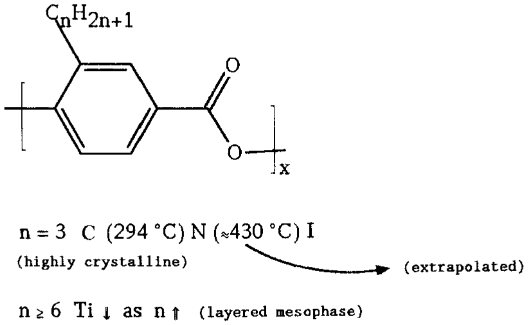


Figure 7. A simple example of a linear polyaromatic thermotropic LCP [3].

A different way to obtain thermally tractable rigid-rod homopolymers is that of utilizing laterally substituted monomers whose terminal bond directions are collinear or parallel to each other. An example of this, to mention just the latest one, is provided by the polymers of 3-*n*-alkyl-4-hydroxybenzoic acid (see figure 7) [3]. Appending a propyl group as a substituent is sufficient to obtain a soluble, thermally processable polymer, still with a high melting temperature (294°C) and a nematic mesophase, whose isotropization temperature has been extrapolated to be as high as ~430°C. The solid phase is highly crystalline. Lower melting and isotropization temperatures are obtained for longer alkyl substituents. However, for substituents longer than pentyl, the polymers are no longer nematic. The mesophase assumes a layered structure only. In any event, as the volume fraction of side chain increases, a decrease in the elastic modulus would be expected.

Of course, this is only one among the many possible ways to increase the melting entropy without breaking the rigidity and linearity of the basic backbone structure.

## 3. Liquid crystalline networks

Let me switch now to network polymers. This is a class of liquid crystalline polymers with a relatively early conceptual birth date and a rather delayed development. An example of a LC network in the swollen state, formed by cross-linking poly($\gamma$-benzyl-L-glutamate) was examined by Samulski as early as 1968 [4]. Cross-linked structures were obtained in 1973 by Strzelecki and Liebert [5] as the result of a thermal polymerization of mesogenic diacrylates or of mixtures of mono- and di-acrylates. The purpose was that of irreversibly blocking the mesomorphic structure of the molten monomers to preserve it at room temperature. Therefore, high cross-link densities were used and the materials obtained may be defined as mesomorphic glasses (see figure 8).

In the frequently quoted short article by de Gennes [6] dated from 1975, the possibility of obtaining liquid crystalline melts from segmented chain polymers was suggested. De Gennes expected the elastic properties of these melts and those of their slightly cross-linked derivatives to be very interesting. In particular, a coupling between thermodynamic state and mechanical action, stronger than expected for networks based on side chain LCPs was foreseen. Curiously enough, while linear, segmented chain, thermotropic LCPs appeared in the literature at the same time as de Gennes' article, the first example of a neat liquid crystalline elastomer appeared in the literature in 1981 (Finkelmann *et al.* [7]), but it was based upon side chain LCPs. Semi-flexible,

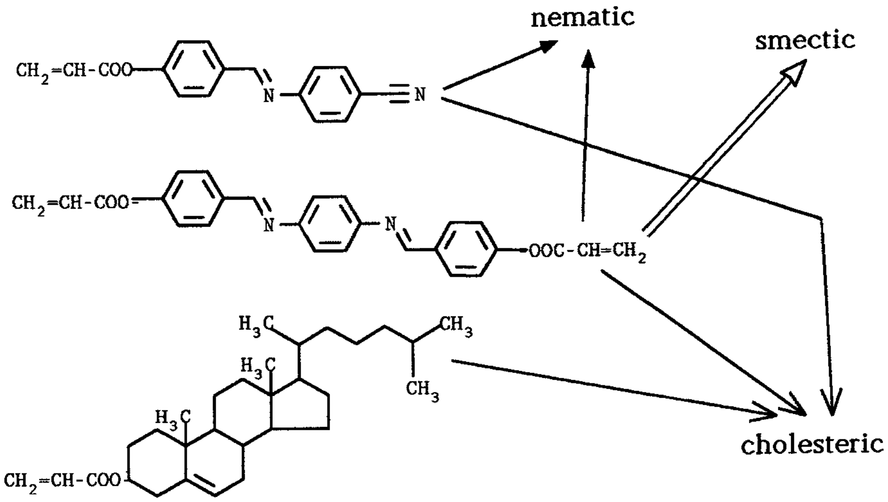


Figure 8. Early examples of networks with liquid crystalline structure [5].

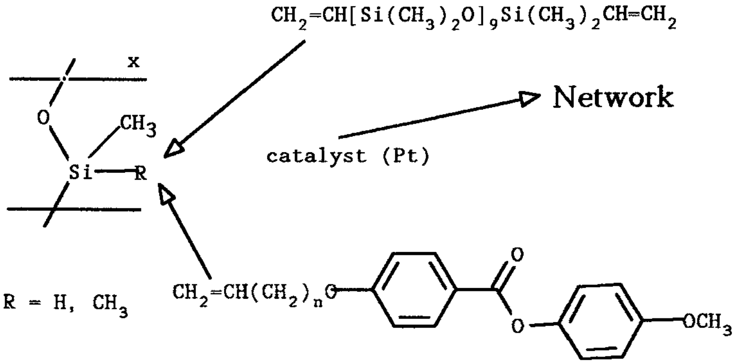


Figure 9. Chemical route to a side chain liquid crystalline elastomer [7].

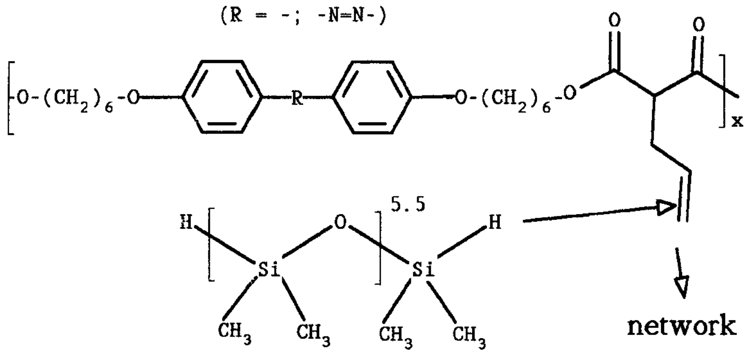


Figure 10. Early examples of liquid crystalline networks from main chain LCPs [8].

main chain-based LC networks followed some years later (1986) through the work of Zentel and Reckert [8].

It would be fair to recall the basic structures for both cases (see figures 9 and 10) Beyond the obvious chemical diversities, a notable difference distinguishing these networks from those prepared by Strzelecki and Liebert is that they undergo a thermotropic phase transition to an isotropic structure, while no such phenomenon occurs with the latter because of their densely cross-linked structure.

During the past few years, interest in this still peculiar class of mesogenic polymers has increased. A valuable effort has been made to define a systematic theoretical frame for their behaviour [9, 10] up to the most recent investigation by Warner and Wang on the phase equilibria of swollen nematic elastomers [11], and some practical applications have also been designed. In 1991 LC networks were the subject of 5·5 per cent of the entire LCPs literature and they had taken a 5 per cent share of the patents (concerning essentially thermosetting materials and composites).

The variety of structures that actually or in principle may be considered for building a LC network is large, ranging from the entirely rigid networks that may be obtained by dense cross-linking of appropriate low molecular weight mesogens (for example rigid-rod diacrylates, following the model of Strzelecki and Liebert) to elastomers containing the mesogenic moieties as pendants in a highly flexible, lightly cross-linked matrix.

Any ordinary cross-linking reaction, starting either from preformed linear polymers or from low molecular weight segments, either in the bulk or in solution, produces LC networks having a polydomain structure. Stable orientation on the macro-scale has been obtained by cross-linking prealigned systems [12, 13]. This may be achieved by magnetic field orientation of the liquid mesophase of low molecular weight mesogens or lyotropic polymer solutions, or by mechanical orientation of polymers in the bulk. A two step procedure for cross-linking (based on the different reaction rate distinguishing the addition of a hydrosiloxane group to alkenic or methacrylic double bonds) has been followed recently by Finkelmann [14] to obtain what he calls a 'single crystal elastomer' (see figure 11).

For LC elastomers, the quest for new chemical structures runs parallel to the investigation of properties such as discontinuous stress–strain response (up to a

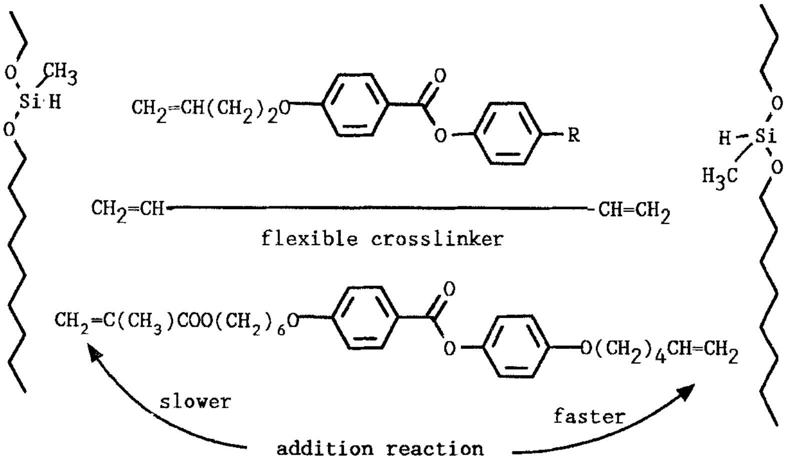


Figure 11. Chemical route to a macroscopically oriented liquid crystalline network [14].

mechanical critical point), strong stress–optical effects, mechanically induced N–I transitions, sample shape changes induced by orientation, properties that make these materials such special systems.

Thanks to the outstanding contribution of Finkelmann and coworkers [15, 16], a consistent experimental picture of some basic properties has been outlined that is in substantial agreement with expectations.

The elastic properties of LC networks have been investigated mostly for side chain polymers. With these structures, a mechanical deformation of the network matrix is coupled with a change in the orientation of the mesogenic side groups in a way for which an explanation is far from being a straightforward matter. Conversely, a change in the orientation of the mesogenic groups driven by a force field reflects in a deformation of the network. The elucidation of the relation between network deformation and mesogen orientation needs accurate experimental data and possibly a detailed description of the phenomenon at the molecular level. A relevant step is the definition of the sense of the coupling, i.e. the relative sign of the order parameters of backbone network matrix and mesogens. This has been done in a few cases. Recently, Mitchell and co-workers [17] have applied small angle neutron scattering techniques to attack this problem for a side chain, polyacrylate-based, moderately cross-linked network and for its corresponding nematogenic linear polymer. In both cases, the order parameters of backbone and mesogens were found to be positive. For the network polymer, a substantial macroscopic orientation of the mesogenic units could be induced by small mechanical extensions and, not unexpectedly, the deformation of the network was found to be non affine. The nematic structure of the assembly of side chain mesogens influences the mechanism of network deformation.

An interesting problem with LC networks concerns the role played by the cross-links relevant to the stability of the mesophase. The point may be better focused for networks which have been formed by the cross-linking of a preformed linear polymer. Some relationship between the isotropization temperatures of homologous linear and network polymers in their dependence on the cross-link density is theoretically expected [10]. If cross-linking is carried out in the liquid crystalline phase, the stability of the latter should be increased, because elastic forces oppose its deformation. On the contrary, for a network obtained from the isotropic state, elastic forces oppose the successive formation of the ordered phase, increasing its free energy and depressing its stability. This effect, that is expected to be of increased relevance the higher the cross-link density and the more rigid the network structure, has been qualitatively confirmed in several cases, although with some exceptions, but its quantitative relevance, with reference to the specific chemical nature of the network has received very little attention. Let me show you an example taken from our own research in the field [18].

The LC network has been obtained by imine formation between a low molar mass diamine and a linear polymer of segmented chain structure containing aldehyde groups as shown in figure 12.

The linear polymer is hardly crystallizable, even by annealing. Melting at ~145°C produces a cybotactic nematic phase stable up to ~300°C. The 10 per cent cross-linked network has almost no crystallinity and its isotropization temperature is definitely lower (~285°C). The structure of the network may be thought of as formed by polymer chains of random copolymeric structure, as shown in figure 13, connected to each other through the flexible oligomethylenic terminal functions.

The presence of =N–PhOR groups, although in a relatively small proportion, modifies the intrinsic mesomorphic properties of the original linear polymer,

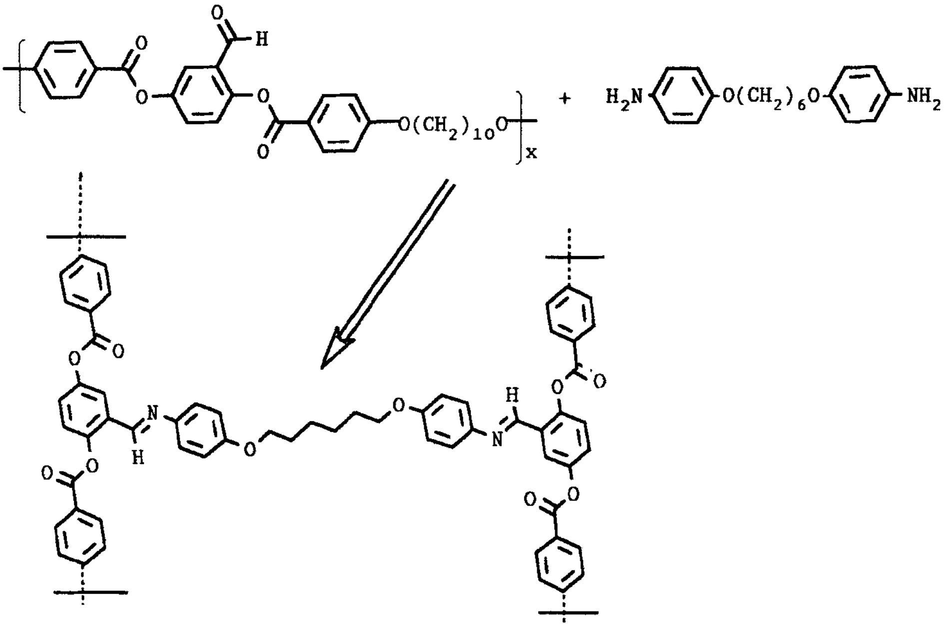


Figure 12. Liquid crystalline network from a main chain LCP [18].

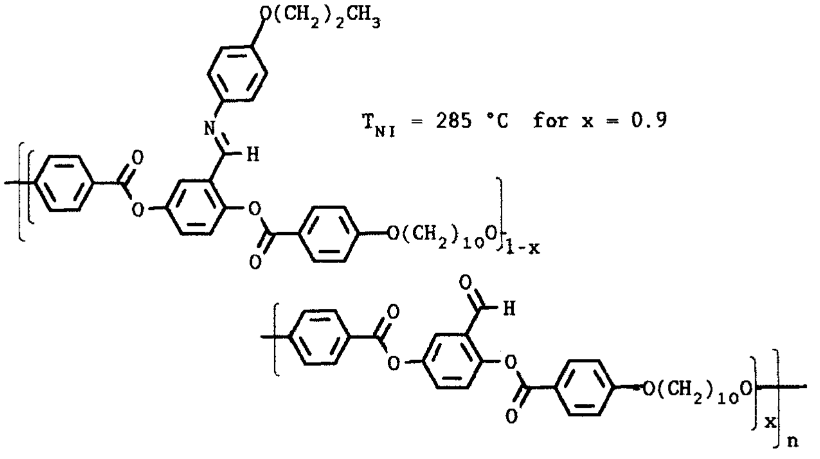


Figure 13. Linear copolymer corresponding to an ‘average’ polymer chain in the network of figure 12 [18].

decreasing the thermal stability of the mesophase ($T_i$ ~285°C). We may consider the polymer as a binary random copolymer formed by monomer units having different mesogenic potentials. The monomer unit containing the iminic branch is ‘less mesogenic’ than the unsubstituted one. This effect may be evaluated by comparison of the mesomorphic behaviour of two low molar mass model compounds, ML and MT, shown in figure 14. Both compounds are nematogenic, but the mesophase of ML is thermotropic with $T_i$ as high as 172·8°C, while MT exhibits monotropic mesomorphism with $T_i$ at 63·8°C.

To mimic the two connected monomer units in the network, two imine substituted units may 'ideally' be connected producing the 'dimeric' compound MH shown in figure 15.

The consequences on the mesomorphic behaviour are small. Like the T shaped monomer, the H shaped dimer is nematogenic, in a monotropic way, but its mesophase stability is about 10°C higher ($T_i = 73{\cdot}1$°C).

In conclusion, at least for low densities of sufficiently flexible cross-links, the reduced intrinsic mesogenic potential of the cross-linked polymer chain appears to be effective in depressing the mesophase stability of the network more than do the interchain constraints produced by the cross-links.

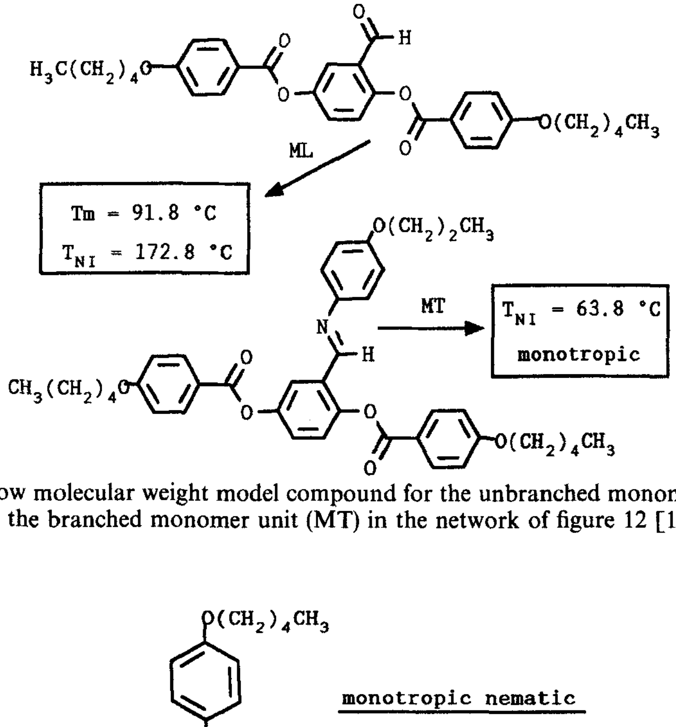


Figure 14. Low molecular weight model compound for the unbranched monomer unit (ML) and the branched monomer unit (MT) in the network of figure 12 [18].

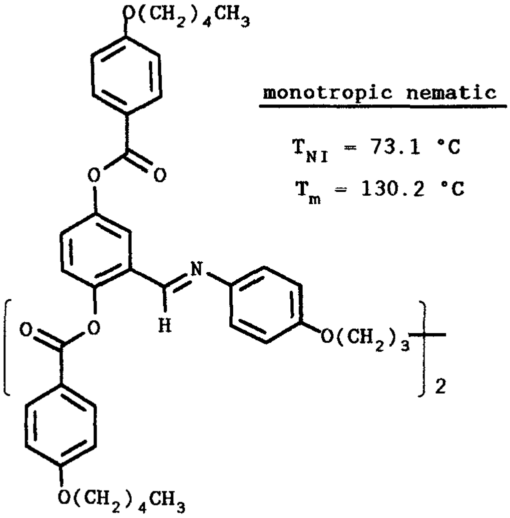


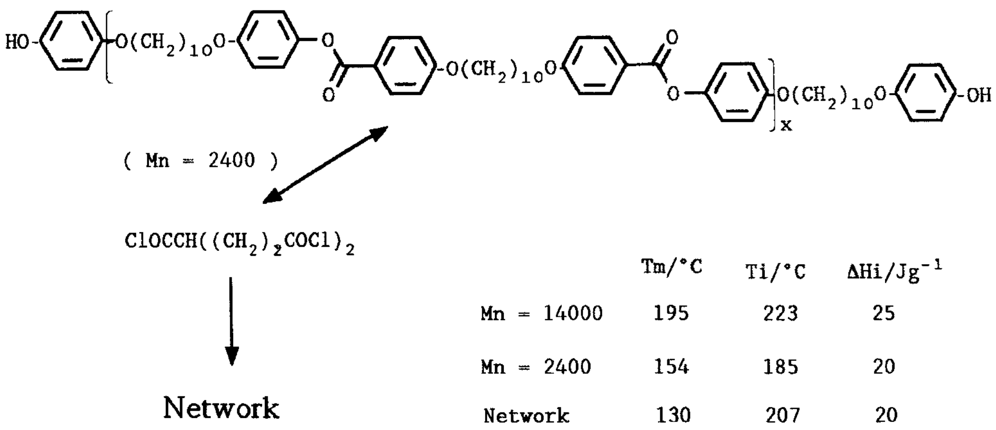
Figure 15. Low molecular weight model compound for two connected branch points in the network of figure 12 [18].

Going back to networks formed in the isotropic phase, a result that is seemingly in contradiction with expectations has been recently reported by Mitchell *et al.* [19] of the University of Reading, England. A liquid crystalline elastomer obtained by cross-linking in isotropic solution a cellulose derivative with a flexible cross-linking material (adipolychloride) exhibits, even for a low (1·6–1·7 per cent) cross-link density, isotropization at a significantly higher temperature than that measured for the uncross-linked cellulose. The authors suggest that some order might have been induced in the reacting sample by the vigorous stirring applied.

A rather different case comes from our own research [20]. A liquid crystalline network was obtained by condensation of an oligomeric polyester with a low molecular weight tricarboxylic acid chloride (see figure 16).

The synthesis of the oligomer, which is a low molecular weight ($M_n = 2400$) variation of a well-known nematic polymer synthesized for the first time by Griffin and Havens [21], was performed in such a way that its chain terminations are –Ph–OH groups. The oligomer is nematic giving isotropization at 185°C, 38°C lower than found for a full polymer ($M_n = 14\,000$). The isotropization enthalpy of the oligomer is 20 $\mathrm{J g^{-1}}$ as compared to 25·4 $\mathrm{J g^{-1}}$ found for the full polymer.

The cross-linked polymer was obtained by reaction in a solution of *o*-dichlorobenzene at 170°C. Under these conditions, the network forms in the swollen isotropic state. The dry network is a semi-crystalline material with a very low degree of crystallinity. Crystallinity fades out above ~140°C and the 'molten' network has a nematic structure. Isotropization takes place around 207°C, i.e. at a temperature which is higher than that measured for the oligomer and lower than that found for the full polymer. Seemingly, in this case, the cross-links play two contrasting roles: that of chain extenders which should favour an increase in the stability of the nematic phase, and that of mechanical constraints between linear chains that should disfavour it. For highly cross-linked networks that form from low molecular weight non-mesogenic compounds, an isotropic structure is normally expected. However, this may not be the case. An interesting and rather peculiar case has been reported by Ober *et al.* [22] concerning the formation of triazine, rigid-rod networks by thermal cyclotrimerization of dicyanate monomers (see figure 17).



| | Tm/°C | Ti/°C | ΔHi/Jg$^{-1}$ |
|---|---|---|---|
| Mn = 14000 | 195 | 223 | 25 |
| Mn = 2400 | 154 | 185 | 20 |
| Network | 130 | 207 | 20 |

Figure 16. Chemical route to a LC network from a LC oligomer, and comparison of thermodynamic data among related chemical species [20].

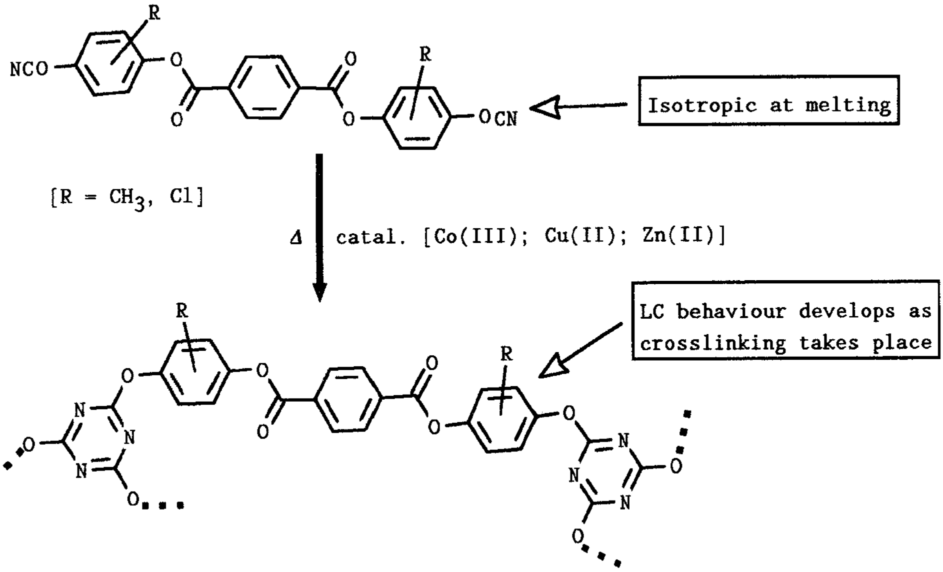


Figure 17. Triazine LC networks from dicyanate monomers [22].

The monomer (actually, a mixture of isomers) melts to an isotropic liquid and mesomorphic behaviour develops only as the thermal cyclotrimerization advances. In this state, some macroscopic orientation may be induced by magnetic action. Finally, anisotropy is frozen into the rigid network.

It is apparent that, as for linear LC polymers, LC networks may be formed by the combination of single molecular groups, none of which is mesomorphic by itself in the molten state.

## 4. Swollen LC networks

Quite reasonably, most of the attention to LC networks has been devoted to exploring the mechanical properties of elastomers in the neat form, and the relationships between these properties and the internal structure. The swollen state of a LC network has received little attention, appearing in many cases merely as an intermediate condition along the route leading to the final cross-linked material. Yet, LC swollen networks can be remarkable systems with interesting properties deserving specific attention. I might summarize the situation in a single sentence saying that a LC swollen network realizes a permeable, self-sustaining anisotropic medium, macro-oriented and chiral structures being possible, whose state of internal order (and shape, in some cases) may be responsive to external and internal (solvent–matrix interaction) forces.

An early example (dated from 1968), of attention paid to a swollen network in the liquid crystalline state is due to Samulski and Tobolsky [4] who utilized a γ-radiation cross-linked sample of poly(γ-benzyl-L-glutamate) as a more practical means of studying the properties of swollen polymer films. Some 18 years later, a significant case of focus brought to bear on a specific property of a liquid crystalline swollen network is due to Zentel [23]. Zentel showed that a network based on a side chain liquid crystalline polymer, swollen in a low molecular weight nematogen, changes its shape anisotropically under the action of an electric field. (The nematic structure of the swelling solvent raises the question as to whether a similar effect could also have been obtained with a non-mesogenic network.)

More recently, the properties of liquid crystalline polymer gels obtained by moderate ($\sim 10$ per cent) cross-linking of poly($\gamma$-benzyl-L-glutamate) solutions have been intensively investigated by Kishi, Sisido *et al.* [24, 25].

A reversible cholesteric–isotropic change paralleled by a helix–coil transition has been observed, as a function of solvent composition and temperature. In a related way, a nematic gel obtained by cross-linking a magnetically aligned polymer solution shows reversible anisotropic swelling as the ratio between helix-favouring component and coil-favouring component of the swelling solvent is changed. Anisotropic swelling means that the cross-linked polymer sample swells or shrinks preferentially along a direction normal to the aligned helical axes, i.e. normal to the field direction. This specific feature is consistent with Samulski's observation concerning the swelling of uncross-linked films reported in 1968 [4].

The phase behaviour of this system is, however, rather strictly related to the structural peculiarities of its ‘mesogenic’ moieties, so that phase changes are more strictly connected with changes in molecular structure than is normally the case with ordinary rigid-rod-based liquid crystals.

A to some extent simpler system has been examined most recently by Mitchell *et al.* [19]. It is based on the cross-linked cellulose derivative mentioned before as having an isotropization transition temperature higher than that measured for the uncross-linked polymer in spite of the fact that cross-linking was performed in an isotropic medium. Consistently, the lyotropic swollen network is found to become isotropic at solvent concentrations higher than measured for the uncross-linked polymer and increasing with increasing cross-link density. The reason for this unexpected behaviour is traced by the authors to a possible orienting effect of the mechanical stirring on the reacting system. The cross-linked polymer might have retained memory of that non-equilibrium state of order.

Networks formed by cross-linked poly($\gamma$-benzyl-L-glutamate) or cellulose derivatives have in common, at least in the liquid crystal phase, the presence of stiff molecular segments of considerable length. Furthermore, for the first system, isotropization is accompanied by a helix–coil structural transformation.

The phase behaviour of networks swollen in isotropic solvents and formed by semi-flexible LC polymers cross-linked in the isotropic state is still largely unexplored. Very recently, however, Warner and Wang [11] have reported a theoretical calculation of the phase diagram for such systems. Equilibrium between nematic or isotropic gel and free solvent is predicted as a function of temperature and composition. A triple point is also expected, with anisotropic and isotropic gel coexisting. Of course, the existence of one phase states (nematic or isotropic gel) as a function of composition and temperature is also calculated.

A corollary of interesting related problems is outlined concerning: networks formed in the LC state; swelling with nematic solvents; effects of elastic distortions at the isotropic–nematic gel interphase, occurring as a consequence of discontinuities of the degree of swelling; effects of an applied stress on the phase equilibria.

Coming to experiments, let me now draw attention to the behaviour of two networks whose structure and preparation procedure correspond to the assumptions of Warner and Wang. They are based on nematogenic, segmented chain polymers and I have mentioned them before with reference to the mesophase stability of the neat forms.

A report [20] concerning the first example has appeared in the literature simultaneously with the article of Warner and Wang [11].

The network is obtained in the swollen isotropic state as it forms at 170°C by reaction of a terminally –Ph–OH functionalized nematogenic oligomer and a tricarboxylic acid chloride. The swollen network becomes anisotropic on cooling. Deswelling occurs up to a solvent concentration of ~74 per cent by weight at room temperature. No trace of crystallinity is detectable in the X-ray diffraction spectrum. The DSC heating curve of a polymer sample in the absence of excess of solvent shows a rather broad endothermal signal peaked at ~87°C. Substantial supercooling affects the reverse transition. In corresponding with these observations, optical isotropization and anisotropization are observed, respectively. In the presence of excess of solvent, the qualitative behaviour of the network is unchanged. A small decrease of the peak temperature on heating and a broader exothermal effect on cooling are detectable. Isotropization is accompanied by further solvent intake, while slow deswelling occurs on cooling. The isotropization enthalpy is 9·5 J g$^{-1}$, corresponding to 36 J g$^{-1}$ of pure polymer.

As to the second example, cross-linking was performed at 105°C using *o*-dichlorobenzene. The solvent/polymer weight ranges between 0·036 and 0·048 according to the polymer preparation procedure, in order to achieve easy stirring of the polymer solution before cross-linking takes place. Under these conditions, the network forms in the isotropic state and the solvent is entirely included in the cross-linked, isotropic, transparent gel. Partial deswelling occurs on cooling to room temperature and optical anisotropy develops. The equilibrium degree of swelling is attained slowly for bulky samples (>10 days at 26°C) at a polymer solvent weight ratio ranging between 0·065 and 0·080, according to the polymer preparation process utilized.

The swollen polymer is a non-crystalline solid with a rubbery consistency. The DSC analysis indicates an endothermal transformation occurring in the temperature range 50–90°C, with an enthalpy ranging between 2·4 and 2·8 J g$^{-1}$ corresponding to 37–39 J per unit mass of unswollen polymer. In correspondence with this, isotropization takes place. Both phenomena are reversible, although not quantitatively on the time scale of the experiment (temperature scanning rate 10°C min$^{-1}$). A qualitatively analogous behaviour, together with an increased swelling, is exhibited by the network in the presence of excess of solvent. In conclusion, the optical and thermal phenomena outlined are simultaneous and mutually related. No data are available as yet to decide about the origin of this behaviour. However, some discussion about possible hypotheses might be helpful.

If we assume that the swollen, optically anisotropic network is a monophasic nematic gel, the thermal and optical phenomena would correspond to the nematic–isotropic phase transition. When the anisotropic network is in the presence of excess of solvent, the equilibrium solvent–nematic gel has to be considered, and the thermotropic phase transformation is accompanied by further solvent intake. This 'simple' hypothesis is contrasted by the low polymer concentration characterizing the swollen network. It may be worthwhile remembering that only for solutions of rigid-rod polymers such as poly(1,4-benzamide) [26] or poly(1,4-phenyleneterephthalamide) [27] have similar critical concentrations for the onset of mesomorphism been found.

In a different hypothesis, the swollen network, even in the absence of excess of solvent, might be considered as a biphasic system whose optical anisotropy would originate from a phase of liquid crystalline 'solid' structure microdispersed in the solvent. In other words, the transition to the optically anisotropic state would coincide, although on a microscopic scale, with a quasi-discontinuous collapse of the network in a way similar to that discussed by Erman and Flory [28]. Conversely, the endothermal effect that accompanies the loss of birefringence would correspond to the solution of this condensed phase in the (isotropic) solvent to form a monophasic isotropic gel.

Preliminary high resolution $^1H$ NMR data concerning both the anisotropic and the isotropic state are in favour of the biphasic model [18]. However, the question about how a microdispersed, but interconnected, 'solid' structure can be compatible with the overall degree of swelling found is still open.

## 5. Polymeric metallo-mesogens

Let me switch now to a quite different subject, namely, polymeric organo-metallic mesogens.

This class of compounds constitutes a relatively small section of the wider, but not yet wide, area of metallo-mesogens. Although a few examples of low molar mass compounds were reported by Vorländer a very long time ago [29], more specific attention to organo-metallics begun some 15 years ago with the work of Malthète and Billard on low molecular weight ferrocene derivatives [30] and that of Giroud and Mueller-Westerhoff on nickel and platinum dithiolenes [31]. However, a quantitatively significant development of metallo-mesogens is no older than 10 years, and, for the most part, is no older than 5 years [32].

Actually, some rod-like conjugated platinum poly(yne) polymers should be considered among the first examples of metallo-mesogens [33, 34] (see Figure 18).

Because of their structure, their liquid crystalline behaviour was observed in the lyotropic form for concentrated solutions.

Why metals, and why polymers? The considerable variety of metal coordination geometries offers good opportunities for building new molecular structures. Metal bonding allows the connection of preformed ligands of intrinsic mesomorphic potential, as well as the formation of mesogenic complex molecules from non-mesogenic ligands. In principle, the formation of chiral complex mesogens having the metal atom as the centre of asymmetry is also possible as, for example, in the octahedral

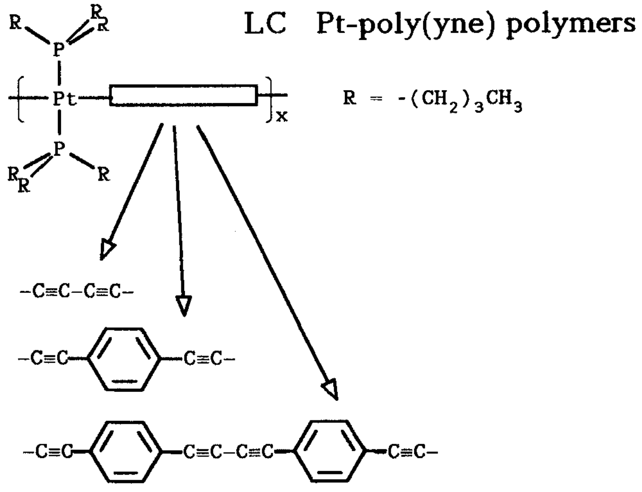


Figure 18. One of the first examples of metallo-mesogens [33, 34].

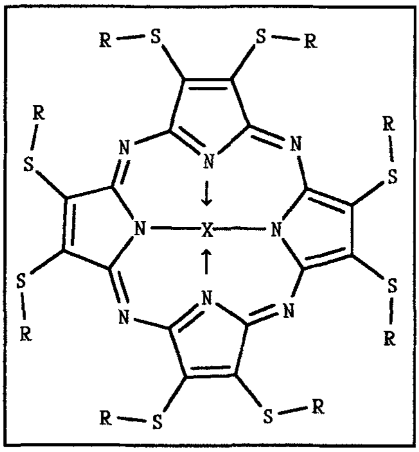
chelation of bidentate ligands or in the complexation of prochiral groups. However, this possibility has not been exploited as yet. Metal atoms in the complex mesogen constitute centres of high local electronic density and polarizability and, in some cases, paramagnetism. These properties are reflected not only in the electronic structure of the single isolated molecule, but also in the mutual interaction between molecules and external fields, including interactions among molecules. The dielectric properties and the colour of liquid crystalline mixtures may be modulated by the presence of variable amounts of a metal-containing mesogen. The presence of the metal atom may have quite remarkable effects on the phase behaviour of a molecular assembly, even in those cases in which the geometry of the complex molecule is entirely defined by the ligand. An example of this, concerning metal complexes of tetra-azaporphyrin derivatives, is shown in figure 19. The stability of the discotic mesophase is enhanced by the metal atom [35, 36].

Why polymers then? The opportunities given by the polymeric structure are the same as for ordinary organic compounds. Polymerization may create or stabilize or permanently fix liquid crystalline order. By means of polymerization, the interaction between specific molecular groups may be favoured and stabilized on the micro- and macro-scales.

An example of noteworthy physical effects produced by polymerization that fixes permanently the liquid crystalline structure of the fluid monomer is shown in figure 20.

The discotic arrangement of the metal phthalocyanine derivative containing acrylate or methacrylate groups at the end of the flexible substituents is fixed by thermal cross-linking. The electrical conductivity of the cross-linked Cu-phthalocyanine was found to be higher than that measured under the same conditions for the analogous unpolymerized compound [37].

Polymerization may provide a means for making permanent certain mixtures of relevant molecular groups to be included in a monophasic LC system, in order to influence some specific physical property. Figure 21 shows the case of a copolymer based on poly(γ-benzyl-L-glutamate) containing a small amount of chemically bound metal phthalocyanine groups. This does not significantly change the structure of the cholesteric lyotropic phase, but influences its light absorption properties [38].



$R = -(CH_2)_{n-1}CH_3$

– Free porphyrin non-mesogenic for $n > 6$

– Metal complexes (X = Co, Ni, Cu, Zn) columnar discotic for $n = 4 \rightarrow 12$

Mesophase highly stable

$$\mathrm{Ti} = \begin{cases} 271\ ^\circ\mathrm{C} & \text{for } X = \mathrm{Co},\ n = 4 \\ 153\ ^\circ\mathrm{C} & \text{for } X = \mathrm{Co},\ n = 12 \end{cases}$$

Figure 19. Mesogenic metal complexes of tetra-azaporphyrin derivatives. Metal complexation enhances the stability of the discotic phase [35, 36].

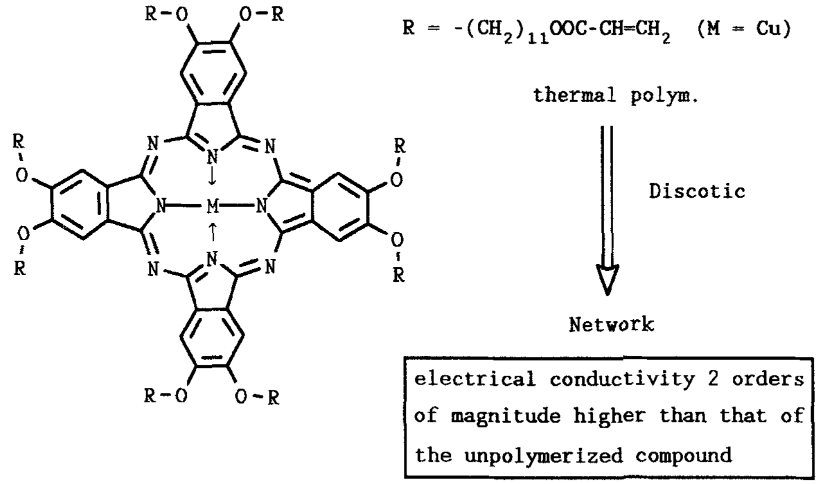


Figure 20. Effect of polymerization on the physical properties of an organo-metallic discotic material [37].

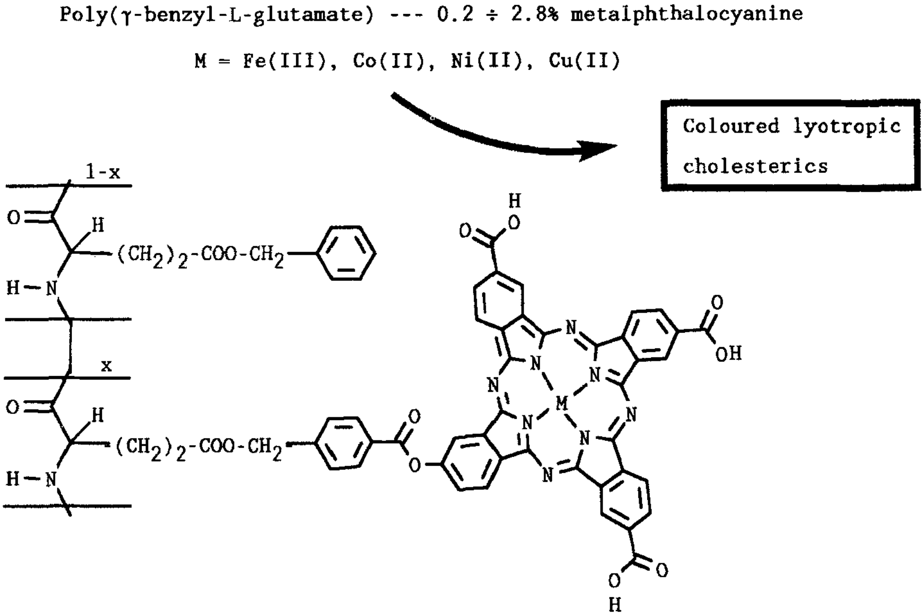


Figure 21. Colour properties of a cholesteric LCP influenced by chemical bonded organo-metallic groups [38].

The synthesis of organo-metallic LCPs may utilize the metal complex formation as the polymerization step. An example of this procedure is shown in figure 22. A dimeric tetradentate mesogenic ligand is polymerized to a linear smectogenic polymer by complexation to copper(II) ions [39].

To some extent, in a similar way, Hanabusa *et al.* [40] utilized metal complexation to cross-link a mesomorphic polymer containing $\beta$-diketonic ligands in the mesogenic side chains. This is shown in figure 23. For moderate cross-link densities, the

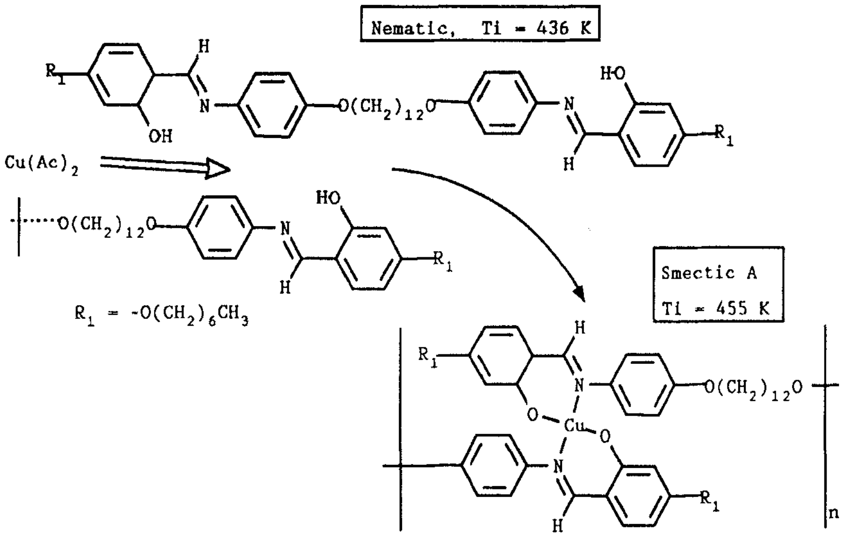


Figure 22. Metal complexation and polymerization to a LCP in a single step [39].

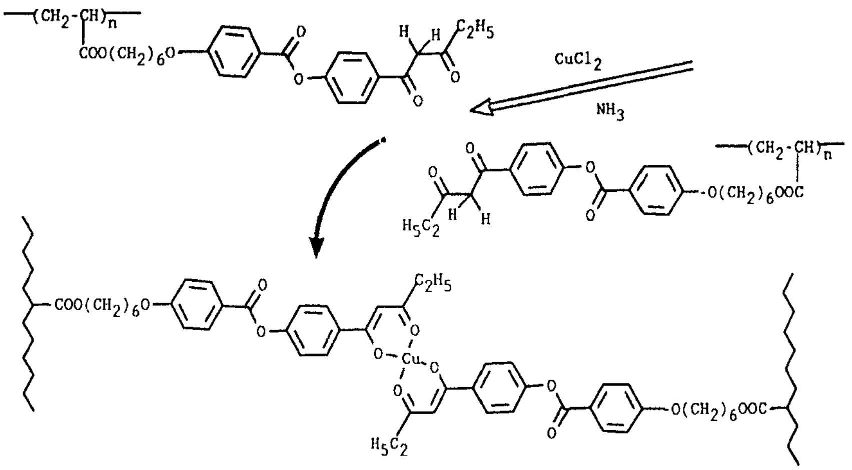


Figure 23. LC network formation by metal complexation [40].

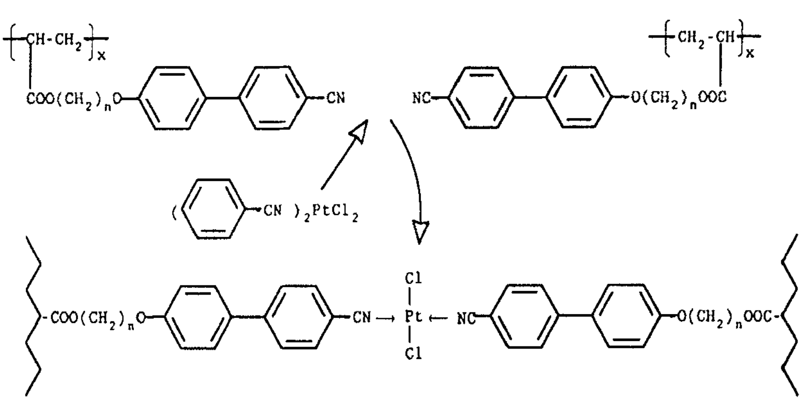


Figure 24. LC network formation by metal complexation [41].

mesomorphic behaviour of the linear polymer is substantially preserved and the transition to the isotropic phase may still take place.

Analogous results have been obtained by Hanabusa *et al.* [41] with a different system in which cross-linking is obtained by complexation of Pt(II) to the 4'-cyano-4-biphenyloxy groups of a side chain mesomorphic polymer. Mesomorphic behaviour is preserved for moderate cross-link densities.

Polymeric metallo-mesogens may also be obtained utilizing performed organometallic comonomers which do not need to be mesogenic themselves. An example of this is shown in figure 25.

The square planar copper complex of the 2,4-dihydroxyphenylalkanimine derivative is not mesomorphic itself. The polymers, on the contrary, are mesomorphic, although in a monotropic way [42,43]. Also mesomorphic are the low molecular weight complexes that may be taken as structural 'monomers' [43]. The polymers have a good chemical stability at high temperatures. Notwithstanding the considerable length of the mesogenic group, melting and isotropization temperatures are tractable. This is most certainly due to the presence of the laterally linked alkanimine groups. This structural feature is also relevant in relation to the nature of the liquid crystal phase. Although the nematic phase is the most stable one for all polymers, its cybotactic tilted structure becomes more pronounced as *n* increases. For *n* larger than 9, a true smectic tilted phase appears.

Even from these few examples it becomes apparent that tractable organo-metallic liquid crystalline polymers are feasible, and that they may be stable enough to allow manipulation.

## 6. Conclusion

As compared to low molecular weight compounds, polymers have become quite recently a quantitatively significant subject in the field of liquid crystals. Some of them, notably those designed for the production of high strength materials, are coming now of age, but attention given to them is still far from being exhausted. Others, like those designed to achieve desired optical and electrical properties, are at an earlier stage of

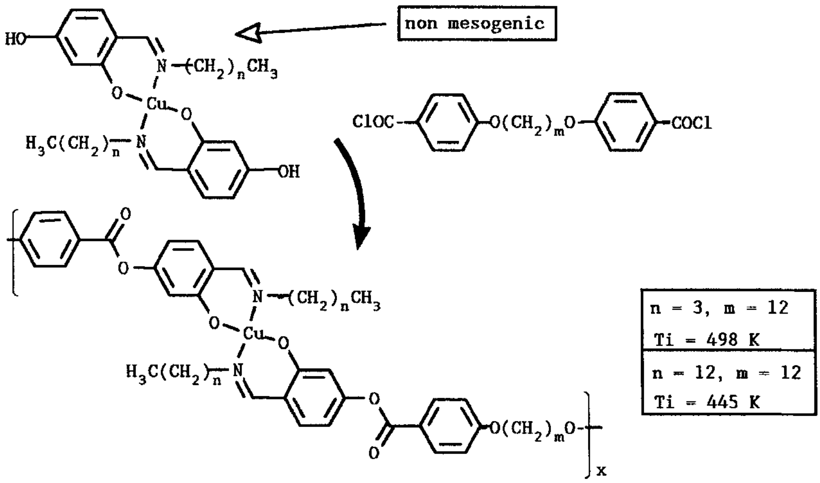


Figure 25. Organo-metallic LCP from a preformed non-mesogenic organo-metallic monomer [42,43].

development and are demanding increasing attention. In this lecture, with deliberate restrictions in scope, polymeric liquid crystals have been considered with reference to (i) a desirable specific physical property, (ii) a peculiar feature of the molecular structure, and (iii) a peculiar feature of the chemical structure. The choice might have been made in many different ways but, in any case, it should have been apparent that no matter whether the primary interest is focused on the exploitation of some specific property or on the investigation of the effects of some specific chemical or structural feature, polymers afford new and peculiar challenges and materials for theoretical and experimental investigation, and powerfully contribute to the enlargement of our knowledge of liquid crystallinity.

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