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INVITED PAPER

MESOPHASES II.

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In the continuation of a review of the classification, properties and applications of mesophases, the general features of thermodynamic data of thermotropic liquid--crystalline phase transitions are surveyed. The orientation of molecules in liquid--crystalline mesophases is discussed in relation to the electrical properties. Some applications of mesophases are outlined. After surveys of both the structural classes of lyotropic mesophases and the properties of plastic crystals in cubic phases, the thermodynamic, structural and other properties of all mesophases are summarily considered in relation to the present state of the knowledge in this field.

In this second and concluding part of the survey of the structures and properties of mesophases, we consider the thermodynamic aspects of phase transitions in both liquid crystals and plastic crystals, the structural properties of lyotropic materials and plastic crystals, and the applications of these varied compounds. The compounds, figures and selected references in this part are numbered in the same sequence as in part I.

THERMODYNAMICS OF THERMOTROPIC LIQUID--CRYSTALLINE MESOPHASE TRANSITIONS

Because many liquid--crystalline mesophases if enantiotropic are thermodynamically stable within certain ranges of temperature and pressure, we can represent the phase properties on a phase equilibrium diagram in the traditional manner, as in figure 2. Of course the region denoted M therein could be subdivided into various approximately vertical strips, one for each individual mesophase of the several possible for a particular compound. At a triple point three phases are present in thermodynamic equilibrium. Because the effect of pressure on the solid and liquid phases and mesophases is commonly relatively small, the lines between these phases are nearly vertical from these triple points if the pressure scale is linear; thus the temperature at each triple point is essentially the same as the transition temperature for the corresponding phase change under atmospheric pressure. For

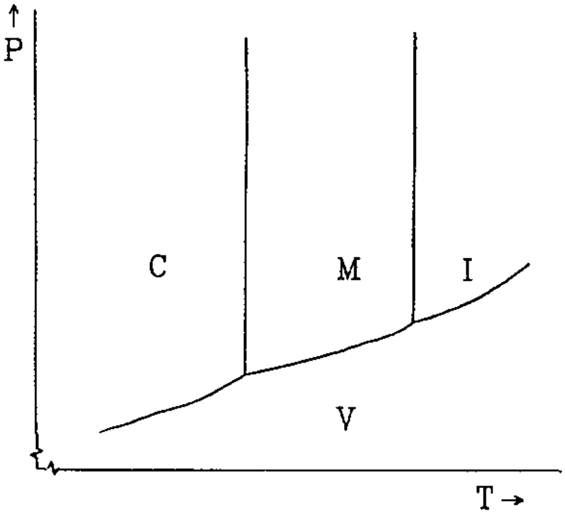
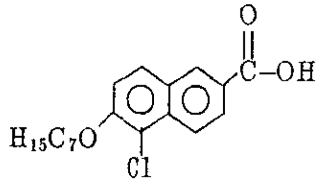


Fig. 2. Diagram of thermodynamic phases for a prototypical mesogen having only one mesophase (M) in enantiotropic equilibrium with true crystalline (C) and isotropic liquid (I), and vapour (V) phases.

4,4'--dimethoxyazoxybenzene (4) at the standard pressure (10^5 N m^{-2}) the crystalline compound melts sharply at 391.5 K to a milky (turbid) and viscous liquid in the nematic mesophase, and at a further sharp transition point 409.2 K to a clear nonviscous liquid. The transition temperature at which the isotropic liquid is formed is known as the 'clearing point'. As with other phase changes, the condition of thermodynamic equilibrium of two phases together is that the change of Gibbs energy $\Delta G = 0$, so $\Delta H = T \Delta S$ at the transition temperature. At the melting point, $\Delta H_m = 29.54$ kJ mol^{-1} and thus $\Delta S_m = 75$ J K^{-1} mol^{-1}; at the clearing point the enthalpy change is only $\Delta H_{cl} = 573$ J mol^{-1} and the entropy change $\Delta S_{cl} = 1.4$ J K^{-1} mol^{-1} is also relatively small[10]. The extent of the entropy increase may be taken as a qualitative indication of increase of molecular disorder; thus the major increase in disorder occurs at the melting point, not at the clearing point. We can thus understand the reason that liquid-crystalline mesophases exist for only molecules having particular shapes and interactions (relatively long and rigid molecules containing polarizable groups or discotic cores with long appendages), and generally within relatively narrow ranges of temperature.

In considering the thermodynamic properties, especially the phase transitions, of mesogens, we recall that the definition of the order n of a phase transition is the order of the derivative of the chemical potential μ (or Gibbs energy G for a pure substance) with respect to temperature or pressure which first becomes discontinuous at the point of the transition. At a first-order transition point, the enthalpy change $\Delta H \neq 0$ and the change of molar volume $\Delta V_M \neq 0$, whereas at the point of a second-order transition $\Delta H = \Delta V_M = 0$ but the thermal capacity $(\partial^2 \mu/\partial T^2)$, the thermal expansivity $(\partial^2 \mu/\partial T \partial P)$ and the isothermal compressibility $(\partial^2 \mu/\partial P^2)$ all undergo discontinuous changes. The melting of a true crystal to a true liquid is a first-order transition, whereas the transition at the lambda point of normal liquid helium to superfluid helium is second order. Most transitions between mesophases are termed weakly first order because ΔH and $\Delta V_M/V_M$ are much smaller than at the melting point. Consequently, large pretransitional effects, comparable with those of second-order transitions, are commonly observed, for instance for the thermal capacity, in the region of the transition point.

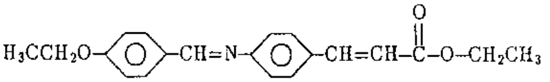
Another compound, 5-chloro-6-heptoxy-2-naphthoic acid (34), has two mesophases. Below 438.65 K it exists in an ordinary crystalline form, but at that temperature it changes to a turbid, viscous melt that adheres to the container; if we spread this substance on a flat surface, we can discern steps or ridges in the upper surface of the material. The material exhibits birefringence (the refractive index is different in directions parallel or perpendicular to the surface on which it is placed, and double refraction is possible), a characteristic of (noncubic) crystals; there are also areas of different colours, due to optical interference effects. At 449.65 K a further transition occurs to a fluid but still turbid liquid, and at 474.15 K true melting to a clear liquid occurs. All these transitions are sharp, each taking place within a temperature interval < 0.5 K. The first transition occurs from a crystalline to a smectic phase, then the next from smectic to nematic, and finally from nematic to the true liquid phase.



(34)

$$(34)\quad T/K \quad C \xrightarrow{438.65} S \xrightarrow{449.65} N \xrightarrow{474.15} I$$

In general, there are known pure substances that exhibit both smectic and nematic mesophases, or both smectic and cholesteric mesophases, but not both nematic and cholesteric mesophases. Whenever both a smectic and either nematic or cholesteric mesophases are known for the same substance, the smectic mesophase always occurs at lesser temperatures, except for the re-entrant nematic phases discussed in I; this behaviour is consistent thermodynamically with the generally greater degree of molecular order in the smectic phase. Analogously, if one substance has more than one smectic mesophase, a progression through the smectic mesophases with increasing temperature generally occurs such that the molecular disorder evidently increases with increasing temperature; however, apparent exceptions to this generalization exist,

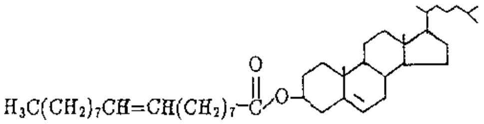


(35)

such as in the case of the re-entrant nematic phases of compound (9). As an instance of multiple smectic phases, we consider the substance ethyl 4-(4-ethoxybenzylidenimino)cinnamate (35) for which the thermodynamic data[10] for enantiotropic transitions are given in Table 1. This compound has a nematic phase just below the clearing point, to which the entropy change from the smectic A phase is relatively large; possibly the unknown smectic phase is smectic E. For comparison, the corresponding thermodynamic data for compound (7) are also given in Table 1; this compound lacks a nematic mesophase, and the entropy change at the clearing point is correspondingly much larger than for (35). The values of ΔH and ΔS for the enantiotropic transitions into the chiral smectic C phases of compounds (30)-(33) are similarly in the ranges 1-3 kJ mol^{-1} and 0.3-0.8 J K^{-1} mol^{-1} respectively[9]. In other cases however, the magnitude of ΔH for a transition between two smectic phases may be characteristic of the nature of the phases between which the transitions occur; evidence from xray diffraction or miscibility measurements for the structures of the phases is still required in such cases to confirm the structural assignments.

Table 1 Phase transitions in (35)

Transition temperature/K	Nature of transition	ΔH /kJ mol^{-1}	ΔS /J K^{-1} mol^{-1}
354	$C \rightarrow S_?$	27.3	77
?	$S_? \rightarrow S_B$	?	?
391	$S_B \rightarrow S_A$	2.1	5.4
429	$S_A \rightarrow N$	5.1	11.9
432	$N \rightarrow I$	0.51	1.2
Phase transitions in (7)			
352	$C \rightarrow S_G$	34.98	99.4
375.85	$S_G \rightarrow S_F$	0.58	1.5
386.95	$S_F \rightarrow S_C$	0.50	1.3
417.15	$S_C \rightarrow S_A$	0.20	0.48
483.15	$S_A \rightarrow I$	11.45	23.7



(36)

As an instance of a system of monotropic mesophases, we consider the substance cholesteryl 9-octadecenoate (36), for which liquid--crystalline mesophases are readily formed in the process of cooling from the liquid state. Supercooling can readily occur between the true liquid and true crystalline states (for substances having no mesophases), or between a liquid-crystalline mesophase and the crystal at temperatures just below the true melting point, but not commonly or for a protracted interval of temperature between the liquid and liquid-crystalline phases or between two liquid-crystalline mesophases; the reason for this behaviour is that relatively small increases of molecular order occur in the cooling process at most specified transitions except that to the true crystalline state, as indicated by the entropy changes. Supercooling to the extent of about 50 K may occur for some mesogens; between the true melting point and apparent freezing point, metastable liquid-crystalline mesophases may be formed (*i.e.* monotropically). For instance, the crystalline cholesteryl (36) ester melts sharply to an isotropic liquid phase at 324 K; on cooling this liquid, we find transitions to two metastable mesophases: at 322 K a cholesteric mesophase is formed, and at 316 K a smectic (probably S_A)

$$(36) \quad \text{T/K} \quad \text{C} \xrightarrow{324} \text{I} \xrightarrow{322} \text{Ch} \xrightarrow{316} \text{S}_\text{A} \xrightarrow{276} \text{C}$$

mesophase is formed.[10] Finally freezing is observed about 276 K (not a sharp transition because different parts of the sample may freeze at somewhat different temperatures).

For the related compound cholesteryl nonanoate, the transition from the cholesteric phase at the clearing point 364.3 K is reversible, with $\Delta H_{cl} = 0.66$ kJ mol^{-1} and $\Delta S_{cl} = 1.8$ J K^{-1} mol^{-1}. However, the crystal of the latter compound on being heated transforms monotropically to the cholesteric phase at 351.7 K whereas the latter phase on being cooled passes to a smectic A phase at 348.6 K wlth $\Delta H = 0.25$ kJ mol^{-1} and $\Delta S = 0.72$ J K^{-1} mol^{-1} before this ester returns to the crystalline condition at a less sharp, lower temperature.[11]

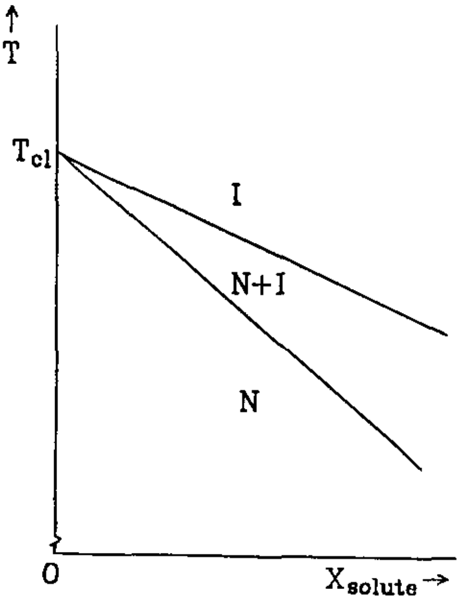


Fig. 3. Prototypical diagram of temperature versus molar fraction of solute for dilute solutions of a non-mesogenic solute in a nematic liquid crystal; T_{cl} = clearing point, I = isotropic liquid phase, N = nematic mesophase, and N+I = two--phase region.

For the discotic mesophases, the transitions in compound (11) with R = $C_6H_{13}S$ from the crystalline phase

$$(11) \quad \text{T/K} \quad \text{C} \xrightarrow{335} \text{D}_\text{o} \xrightarrow{343} \text{D}_\text{d} \xrightarrow{366} \text{I}$$

through two discotic phases D_o and D_d to the isotropic liquid involve the enthalpy changes ΔH/kJ mol^{-1} = 31, 22 and 9 whereas the entropy changes are ΔS/J K^{-1} mol^{-1} = 93, 64 and 25 in order of increasing temperature of the transitions respectively[8].

For binary mixtures of a nonmesogenic solute in a liquid-crystalline mesophase, the temperature for the transition from the isotropic liquid to the nematic mesophase is decreased relative to the pure mesophase, with few exceptions. The presence of impurities (at small molar fractions, $x_{solute} < 0.05$) leads to a region of two phases, as thermodynamically expected if $\Delta H = 0$ and $\Delta V_M = 0$ for the phase change from liquid to nematic mesophase; a partial diagram for the phase equilibria as a function of molar fraction of solute is shown[5] in figure 3.

LYOTROPIC LIQUID-CRYSTALLINE MESOPHASES

Although the term lyotropic implies solvent-induced mesophase, in fact many amphiphilic mesogens that are capable of forming such mesophases in the presence of solvent (commonly, but not exclusively, water) also form mesophases in a pure condition, within appropriate ranges of temperature. The amphiphilic mesogens contain two contrasting groups, a nonpolar hydrocarbon portion and a polar head that tends to bestow solubility in water. Some characteristic polar groups comprise the anionic kind, such as carboxylate or sulphonate, the cationic kind, such as quaternary amine salts, and the nonionic kind, containing the amino group NH_2 or repeated -CH_2CH_2O- links. A requirement of the hydrocarbon portion that is practically without exception is that the alkyl group, characteristically unbranched, must contain at least eight carbon atomic centres .

The major interests in lyotropic mesophases have been related either to the applications of these mesogens as detergents, although their function as detergent operates at solute concentrations much smaller than those of any mesophases, or to the similarities of their properties to those in biochemical systems, in particular to the living cell and its membranes. It suffices for the present purpose to introduce the principal structural types in these mesophases and to compare these with the thermotropic liquid crystals[12,13].

The similarity between the smectic D mesophase and spherical micelles of, for instance, sodium dodecyl sulphate in water at concentrations somewhat greater than the critical micelle concentration has already been noted; both these spherical micelles and the smectic D mesophase are optically isotropic. However if a little water is added to the same solid sodium dodecyl sulphate salt, a lamellar mesophase is formed resembling the interdigitated smectic A_d type, with water molecules and Na^+ cations between the polar heads of the sulphate anions that form the layers having the alkyl appendages within. In the cubic or viscous isotropic phase, the layers are curved to form spherical units having the alkyl groups within the spheres; these units form a body-centred cubic arrangement with water and Na^+ cations occupying the space between the spheres. The *third structure is the columnar or hexagonal phase in which* the layers are rolled into cylinders of indefinite length; these cylinders form columns in an hexagonal array resembling one structure adopted by the discotic mesogens. It is also possible to have inverted hexagonal or viscous isotropic phases in which the water is trapped inside the cylinders or spheres, respectively, and in which the alkyl groups are directed outward. Cholesteric liquid crystals may be formed by solutions of polypeptides in organic liquids, such as trichloromethane or dioxane, within certain ranges of concentration[10].

Electric and magnetic fields and mechanical deformations have practically no effect on many lyotropic liquid-crystalline mesophases. However, those systems, in general having components numbering more than two, that are oriented by a magnetic field and by flow are called lyotropic nematic mesophases[14]. The latter adopt either the columnar structure described above, or a related one that may be envisaged as a cylindrical bilayer having the alkyl appendages parallel to the axis of the cylinder.

As an instance of an amphiphilic mesogen that is capable of forming mesophases in both the pure and aqueous solution states, we mention the alkylated carbohydrate dodecyl maltoside; this compound forms a thermotropic smectic A phase that is also miscible with water so producing lamellar lytropic mesophases[15].

ORIENTATION IN LIQUID-CRYSTALLINE MESOPHASES

The orientation property of these mesogens in the mesophases gives rise to interesting phenomena pertaining to alignment under various conditions. For instance, for the *substance 4,4'-dimethoxyazoxybenzene (4) in its nematic* mesophase, the application of an external magnetic field of moderate flux density (~ 3 teslas) causes alignment of the molecules in the bulk of the sample with their long axes *parallel to the direction of the magnetic field; this* alignment persists for several minutes after removal of the magnetic field. Thin films of this substance between glass plates can be oriented by boundary effects; rubbing the glass surfaces together leads to 'planar layers' in which the long axes of the molecules are in the plane of the film and in the rubbing direction. If the glass surfaces are carefully cleaned (with mixtures of sulphuric and chromic acids, for instance), then 'erected layers' may be obtained in which the molecular long axes are perpendicular to the plane of the film. In all cases the intermolecular interactions lead to a tendency of a parallel alignment of the long axes of adjacent molecules, whereas the thermal (or brownian) motion of the molecules opposes this alignment. The latter effect eventually prevails in the true liquid state at temperatures above the clearing point.

Because the materials in some mesophases exhibit birefringent optical properties--*i.e.* the refractive index differs in the directions parallel to and perpendicular to the director, one expects that the electric permittivity also has different values in these two directions[16]. We can denote these two principal values $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ respectively; then the difference $\Delta\varepsilon \equiv \varepsilon_{\perp} - \varepsilon_{\parallel}$ is the value of the dielectric anisotropy. The sign of $\Delta\varepsilon$ is extremely important: if $\Delta\varepsilon$ is $>$ 0 then the director tends to align parallel to the applied electric field, but conversely if $\Delta\varepsilon$ is <0 then the director tends to be perpendicular to the applied field. The alignment properties in magnetic fields depend analogously on the relative magnitudes of the principal components of the molecular magnetic susceptibilities. Consider a nematic mesophase between two glass plates. Assume that the director is parallel to these plates; this condition can be achieved by suitable treatment of the glass surfaces. Let an electric field be applied perpendicular to the plates. If the dielectric anisotropy $\Delta\varepsilon$ is <0, the field reinforces the existing position. In contrast, if $\Delta\varepsilon$ is >0, the field tends to orient the director perpendicular to the glass plates. The mechanism is as follows. With only weak fields, no effects are observable; there exists a certain threshold value of the electric field such that only when this value is exceeded is the director drawn slowly from its original orientation. The application of an even more intense field rotates the director parallel to the field. This phenomenon is explained in terms of the mechanical or deformation energy required to make the director alter its orientation[16,17]. An orientation layer (in contact with the glass) normally tends to hold the director parallel to the plates; the applied field therefore needs to be strong enough to overcome this alignment, and the required strength depends on the dielectric anisotropy and the elastic properties of the mesogenic material. In summary, the position of the director is strongly influenced by both the applied electric field and the orientation layer; the combination of these effects is applied successfully in the modern technology of liquid crystal displays.

APPLICATIONS OF THERMOTROPIC MESOGENS

There are many applications of liquid-crystalline mesogens, mostly related to their special optical properties. For instance, in the direction of the axis of rotation of the cholesteric substances, polarised light is reflected, giving rise to bright visible colours. Because the pitch of the rotation varies with temperature, so does the colour: thus thin films of these substances can be used as detectors of either infrared or microwave radiation. Alternatively the temperature distribution of a surface may be determined, for instance, in order to detect both the presence and the size of tumours near the skin by their abnormal biochemical activity that produces locally a relative heating effect. Both sterol and nonsterol cholesterogens are naturally of interest in the latter application of surface thermography; in both cases the sensitivity of colour response to temperature is closely related to the onset of smectic properties at the end of the range of temperature in which a sharp response is desired. As an actual example of this application, a mixture twenty per cent (by mass) cholesteryl ethanoate and the remainder cholesteryl nonanoate changes its wavelength of maximum scattering from yellow to violet in the temperature range 293--350 K[11].

A mixture twenty per cent (by mass) cholesteryl chloride and eighty per cent cholesteryl nonanoate changes from its normal green colour (at 300 K) to red, if benzene is absorbed, or to blue if trichloromethane is absorbed. This application provides a sensitive method of detecting even traces of these toxic vapours[10].

If liquid-crystalline mesogens, especially nematic and cholesteric mesophases, are used as the stationary phase in gas-liquid chromatography, it is found that selective discrimination on the basis of molecular shape is obtained, rather than on the basis of molar mass (within a homologous series of chemical compounds) or molecular polarity (for comparable members of different series) in the case of more conventional stationary phases[18]. Thus the positional isomers of disubstituted benzene compounds have been separated by this method; the otherwise difficult separation of 1,3- and 1,4-dichloro derivatives has been readily accomplished, with the 1,4- isomer being preferentially retained, or analogously the separation of polyaromatic hydrocarbons in the analysis of tars resulting from smouldering floral matter. The combination of the negligible vapour pressure of liquid-crystalline polymers at elevated temperatures and their anisotropic properties results in greater separation efficiencies than conventional materials[3]. Both neat and admixed mesomorphic polysiloxanes have been used as stationary phases in gas chromatographs with open-tubular columns[19]; in this case the side-chain polymers gave a nematic mesophase that was expected to function more efficiently than a smectic mesophase. Furthermore mixtures of enantiomers may be separated on a chiral stationary phase, because transitory diastereomeric complexes are formed between the stationary phase and each enantiomer within a column; the enantiomer forming the less stable complex elutes the more rapidly. If the chiral stationary phases are also mesophases, then improved flow conditions and hence more rapid separations may be attained.

Nematic mesophases are versatile solvents in studies of molecular structure by nuclear magnetic resonance[20], and in other spectroscopic investigations. In the former case the anisotropic components of the spin-spin interactions are easily observed because of the orienting effect of the solvent, whereas the fluidity of the solvent prevents the great broadening of lines generally observed in the crystalline state. For purposes of n.m.r. spectroscopy thermotropic nematic solvents are useful for lipophilic (or nonpolar) solutes, whereas lyotropic nematic solvent systems are preferable for other solutes[14].

Great current interest in liquid-crystalline substances is reflected in biochemical investigations. That many 'liquid' tissues, such as muscles, tendons, nerves and organs, show double refraction has long been known. Although the existence of this property does not imply that these tissues are composed, in part or in whole, of liquid-crystalline substances, it is clear that certain mesophases constitute useful model systems for the study of biochemical properties under simplified conditions[1]. About 1860, tiny fatty globules from the suprarenal gland were found to exhibit double refraction under polarized light. These myelin bodies, as well as esters of cholesterol, ammonium octadecanoate etc., have the power to dissolve other substances to a limited extent, whilst maintaining their mesomorphic character. Other aspects of biochemical cells, such as membrane bilayers, also seem related to properties of liquid-crystalline mesophases.

Electronic devices with rapid switching properties have been based on the ferroelectric properties of mesogens having a chiral smectic C phase[21]; compounds (30)-(33) are instances of this type that were investigated[9] for that reason. Another compound having a ferroelectric smectic C mesophase near ambient temperatures as well as smectic A and cholesteric phases below the clearing point at 364 K, was also found[22] to have useful electromechanical response characteristics.

The best known technological application of liquid crystals is in electro-optic devices for display purposes. For several years liquid-crystalline displays have been used for digital watches and calculators, and more recently large displays have been commercially marketed in portable computers and television receivers. Generally these devices contain mixtures of liquid-crystalline substances in order to maintain the desired properties over the required range of temperatures near ambient. At present the mesophases commonly used[16] are of the nematic type, between two solid substrates that have orientation layers perpendicular to each other, in the so called 'twisted nematic' effect. In the near future the latter effect is likely to be replaced by a different nematic effect in which the director exhibits a rotation, instead of $\pi/2$ in the twisted nematic effect, of $3\pi/2$ radians; this increase is achieved by the addition of a small proportion of chiral substance to the mesophase. Furthermore, the conductors by which the electric field is applied are coated with a layer that tends to align the director at an angle about $\pi/6$ radians to the glass plates. This effect produces a much better contrast for blue on white, and is virtually independent of the viewing angle. Further into the future, electronic displays will probably operate with smectic liquid crystals[16].

PLASTIC CRYSTALS

The possibility that molecules might rotate within a crystal lattice was first proposed[23] by Simon and von Simson in 1924 in order to account for the transition in crystalline ammonium chloride of one solid phase into another. In a further contribution to this idea, Pauling in 1930 recognized[24] that molecular motion in solid phases could be related to the thermodynamics of transitions between two solid phases of various inorganic compounds. The modern concept of plastic crystals originated about 1938 when Timmermans realized[25,26] both that many polymorphic compounds have a remarkably small entropy of fusion, and that the solid phase immediately below the melting point has a high crystallographic symmetry. He described the molecules of these compounds as globular, either being highly symmetric (CH_4, CCl_4) or producing an effectively spherical shape by rotation about an axis (cyclohexane, camphor). Thus Timmermans concluded that these globular compounds constituted a new mesomorphic state of aggregation, intermediate between typical solid and liquid phases. About 1948, Michils observed[27] that some solid compounds composed of spherical molecules can be made to flow through a small hole (extrusion) by means of the application of moderate pressure. Since that time, some organic compounds have been discovered that are so plastic as to deform under their own weight[28]. The pure substance dodecafluorocyclohexane shows extreme plasticity: at room temperature its crystals flow like pitch.

Thus there are solid substances, still crystalline materials, that show one or more transitions between solid states for which no gross rearrangement of the contents of the unit cell (or of the molecular conformations) is discernible. Like the transitions between the liquid-crystalline mesophases, these transitions are easily detected by measurements of thermal capacity, for instance by differential scanning calorimetry, as well as by means of xray diffraction, and spectroscopic measurements (infrared absorption or Raman scattering due to either lattice vibrations or intramolecular vibrations, or nuclear magnetic resonance). Commonly these substances melt at much greater temperatures than expected, but the entropies of fusion are relatively small[29]. For instance, cyclopentane has solid-solid transitions at 122 and 139 K, well below the true melting point 179 K; for comparison the melting point of pentane is 143.4 K. For cyclohexanol, the transition (freezing) from the isotropic liquid to a cubic solid phase that can be cut easily with a spatula, without fracture, takes place at T_f = 299 K, but the entropy of fusion at that temperature is only 5.8 J K^{-1} mol^{-1} (to be compared to the value 55.7 J K^{-1} mol^{-1} for $C_{10}H_8$) and the change of molar volume is also relatively small; in contrast at 265 K this compound undergoes an abrupt and relatively large change in molar volume in a transition to another, brittle solid phase, that can be easily powdered, for which the entropy change (again for the process toward greater temperature) is 31 J K^{-1} mol^{-1}.

Because of the small entropy of fusion, there is at least one practical application of these plastically crystalline compounds: the coefficient for the freezing-point depression $K_f = MR_gT_f/\Delta S_f$ is relatively large, about 40 K for camphor relative to 1.86 K for water; here M denotes the molar mass of the solvent and R_g the ideal gas constant. Ethane, hexafluoroethane, neopentane, cyclohexane, 1,4-dichlorobenzene, hexafluoroplatinum and 2-methyl-2-chloropropane are among other substances displaying plastic-crystalline properties[29] One specific family of compounds that is worth mention is the hydrogen halides, HF, HCl, HBr, HI, plus H_2S but not H_2O. In this plastic condition these substances can be neither easily cleaved nor converted into powders. The substances that exhibit the properties of plastic crystals consist commonly, but not universally, of almost globular molecules; in fact, plastic states of many substances, which are composed of molecules having relatively low symmetry--apart from the plastic crystals of the liquid-crystalline kind that have three-dimensional order, are now known[30]. The premelting phenomena indicated by solid-solid transitions of these substances are related to the onset of molecular motion, such as reorientation (but not free rotation) about only one molecular axis as in the case of cyclopentane, or about other axes in the case of the more globular molecules, but the solid lattice prevails. Thus the more modern appellation to describe such a state of these compounds is a dynamically disordered crystalline solid. This ability to reorient or to adopt equivalent positions with respect to space-fixed axes is characteristic of molecules in the fluid phases (liquid and gaseous). Despite such reorientation (impulsive turns by $\pi/3$ radians 10^5 times per second at 100 K) of the benzene molecule about its six-fold axis of symmetry, onsetting about 90 K-far below the melting point at 279.7 K-according to the great decrease of the linewidth in the nuclear magnetic resonance spectrum[29], apparently benzene is considered not to be a plastic crystal. For comparison, the quasi-isotropic reorientation of adamantane is analogously observed in its n.m.r. spectrum at 143 K, although the transition from true solid phase to plastic crystal occurs at 209 K, also far below the melting point 542 K.

Commonly these substances in their plastically crystalline phases have cubic unit cells (simple or primitive, face-centred, or body-centred), with the length of the unit cell in the range $(0.6\text{-}1.0)\times10^{-9}$ m; in contrast, the potential unit cells of liquid-crystalline phases would have at most a tetragonal symmetry for the smectic A, B and E phases and rhombohedral for the smectic C, F, H and G phases, and would have much larger dimensions. For instance, the melting point of CD_4 is 89.78 K and the entropy change there is only 10.11 J K^{-1} mol^{-1}; there are two λ-type transition points[1] at 27.2 and 22.4 K denoting second-order transitions, and the phase III existing below the latter temperature is tetragonal. Within its phase I CD_4 seems to be partially ordered at 77 K but completely disordered at 35 K; the partial ordering apparently reflects the more rapid reorientation processes at the greater temperature. In contrast, in phase II, also face-centred cubic, of the eight molecules per unit cell at 24.3 K six are relatively ordered, but the remaining two are orientationally disordered with almost free rotation[29,30]. As a consequence of the cubic symmetry, the refractive index of the plastic crystals in these cubic phases has generally the same value in a direction parallel to any side of the unit cell, and this value is much closer to that of the refractive index of the isotropic liquid than to that of the more typical, brittle crystalline phases at much smaller temperatures. As another instance, below the melting point of CCl_4 at 250.4 K, there are known to exist a metastable face-centred cubic phase Ia that melts at 245.4 K and a rhombohedral phase Ib that is stable between 225.4 and 250.4 K, with a monoclinic phase at smaller temperatures; in the cubic phase the birefringence is extremely small but apparently finite, whereas in the rhombohedral phase it has a larger value but still much smaller than that of the monoclinic phase[29]. These plastically crystalline materials are generally transparent and colourless, but, having a much larger vapour pressure than typical solid substances, sublime easily. If we compare the changes of the thermodynamic properties thermal expansivity and molar thermal capacity C_p, like the changes of enthalpy, entropy and molar volume, at the true melting point and at the solid--solid transition at lesser temperature, we find in all cases of these plastically crystalline substances that the changes at the melting point are much smaller than those at the other transition temperature bounding these mesophases[31]. Analogously, because of the relative ease of molecular reorientation in this phase, the electric permittivity of a polar compound like cyclohexanol changes only slightly at the melting point, but to a much greater extent at the lower transition temperature. Studies of molecular diffusion by means of the technique of radioactive tracers have demonstrated that the self-diffusion coefficient in plastic crystals can be several orders of magnitude greater than that in ordinary crystals; this diffusion may be associated with an entropy due to vacancies, in the range 37-75 J K^{-1} mol^{-1} for plastic crystals, to be compared with 130 J K^{-1} mol^{-1} for benzene. For instance for cyclohexane at the melting point, the value of the self-diffusion coefficient is $\sim 10^{-9}$ m^2 s^{-1}, nearly 10^6 as large as that of naphthalene[31].

Plastic crystals are one of three classes of solid compounds having relatively large molar entropies. For the plastic crystals or dynamically disordered crystalline solids, the excess entropy beyond the rotational and vibrational entropies is mainly configurational, leading naturally to another thermodynamic transition at lesser temperatures with a zero configurational entropy in conformity with the third law of thermodynamics. The second class includes compounds such as ammonium salts, nitrates of alkali metals, esters of long-chain unbranched alkanoic acids etc. that possessing a certain degree of molecular freedom within hard and brittle phases (characterized by sharp xray diffraction patterns) are referred to as rotor-phase solids. Orientationally disordered solids such as ice and ice clathrates within which the molecules lack rotational freedom constitute the third class[32].

DISCUSSION

It must be obvious to the reader of the preceding sections that there is well established to exist a fifth state of aggregation of matter, the mesomorphic state; like the crystalline state that includes seven crystal systems, fourteen Bravais lattices etc., the mesomorphic state actually represents a great range of phases of both chemical substances and their mixtures that have some properties characteristic of both solid (crystalline) and liquid (amorphous, fluid) phases. The distinction most characteristic of a crystalline substance is the anisotropy of its properties, such as optical, electric or magnetic properties. Just as there exist crystals, specifically of the cubic system, for which such properties (although not properties related to mechanical deformation) are necessarily isotropic by virtue of symmetry, there are many classes of mesophases that likewise exhibit isotropic properties; these include the dynamically disordered crystals (or plastic crystals), the smectic D phase, the cholesteric blue phases[33] and the viscous isotropic lyotropic phase, among others[34]. The dynamically disordered cubic crystalline phases are typically adopted by globular molecules, or molecules that become effectively spherical by means of relatively unhindered rotation about some molecular axis, but by no means by only molecules of such shapes. For molecules that have shapes distorted from spherical towards either prolate or oblate ellipsoids, there exist the liquid-crystalline mesophases for lath-like (effectively cylindrical) or discotic[35] molecules, respectively. The diversity of molecular shape is reflected in the diversity of not only classes of mesophases but also their sequences depending on temperature and concentration for particular compounds or mixtures. As discussed above, the distinction between lyotropic and thermotropic liquid crystals is somewhat artificial, just as liquid crystals also constitute plastic crystals under certain conditions. Within the nematic group of mesophases, there exist not only achiral nematic (having parallel directors) and chiral nematic (or cholesteric, having helically varying directors) phases within particular domains, but also both uniaxial N_a and biaxial N_b nematic phases are now known both for pure mesogenic substances and their mixtures[6] and for lyotropic mixtures[14]. Moreover re-entrant nematic mesophases exist in ranges of temperatures below those at which smectic states are stable; although variations in the short-range structure and transport properties exist, the long-range physical properties of the re-entrant nematic phase are identical with those of the nematic phase just below the clearing point[36]. In addition, some cholesteric substances exhibit the fascinating blue phases[33]. Certain mixtures, commonly containing decanol or octanol which are themselves not intrinsically mesogenic, that are conventionally described as lyotropic mesophases also exhibit nematic characteristics, signifying order over a long range in one dimension[14]. Smectic mesophases, numbering at least a dozen, exhibit long--range order in either two (S_A, S_C, S_F, etc.) or three dimensions (crystal S_B, S_E, S_G, S_H, etc.). The discotic mesophases, apart from the nematic phases also exhibited by some discotic mesogens, offer further diversity among the many classes of mesophases.

The *macroscopic process of fusion from an ordered* crystalline solid material to an amorphous isotropic liquid involves the gain by the molecules therein of degrees of freedom beyond those associated with the crystalline state, namely rotation and translation. If the rotational freedom is gained before fusion, then in broad terms the plastic-crystalline mesophases result, whereas if the translational degree of freedom is gained before the rotational degrees then the liquid-crystalline mesophases result. In all cases the reduced entropy of fusion, $\Delta S/R_g$, at the temperature of transformation to an isotropic liquid is much smaller than that of fusion[11] of the noble gases ($\Delta S/R_g \sim 3.34$ for Ne--Xe). For instance the values of this ratio are for SiH_4 1.8, CF_4 2.0, CH_4 2.47, CD_4 2.42 for some compounds forming plastic crystals, to be compared with values in the range < 0.5 for the transitions from cholesteric or nematic liquid crystals, and < 3.0 for smectic A liquid crystals[37]. These values may be further compared both with an average value ~ 8.2 for organic compounds lacking mesophases, and with the value equivalent to Trouton's rule, $\Delta S_v/R_g \sim 11$, for the process of vaporisation of a liquid at its standard boiling point.

The diversity of classes of mesophases is matched by the diversity of the shapes and sizes of molecules that exhibit these properties. Of the shapes we have already commented above on the archtypical distinction between globular, rod-like and discotic molecules. As for size, the dynamically disordered crystals contain[29] some simple molecules, such as the diatomic hydrogen halides and surely including H_2 itself which undergoes practically unhindered rotation within its crystal lattice even at cryogenic temperatures ($< 12K$); commonly the unit cells have relatively small dimensions and high symmetry (cubic or rhombohedral). That these dynamically disordered crystals are also formed with compounds of low molecular symmetry, such as 2,3-dimethylbutane, must not be neglected. Furthermore the dynamic disorder in some three-dimensional liquid crystals makes these solids just as plastic as those *containing "globular" molecules such as adamantane,* despite their monoclinic structures.

A further extension of the properties of liquid-crystalline mesophases depends on the development of further types of chemical compounds. In this review we have relatively neglected polymeric mesogens, firstly because they have been recently the subject of a general review[3], and secondly because the structural principles in relation to their properties are less clear at present than for compounds of smaller molar mass. However, two recently reported polymers containing silicon merit cursory description. The first[38] is a silicone polymer

$(H_3C)_3Si(OSi(CH_3)(CH_2)_4OC_6H_4OC(O)C_6H_4OCH_3)_{35}OSi(CH_3)_3$, having a molar mass about 12.8 kg, with the characteristic 4-methoxyphenyl group terminating the recurring side chains along the siloxy skeleton; on being warmed from a glass at 280 K this compound transforms first to a smectic A mesophase, then to a nematic mesophase at 345 K before reaching the clearing point to an isotropic liquid at 374 K. The other polymer[39] is poly(dihexylsilane) which exhibits liquid-crystalline properties above 315 K, including optical birefringence. In a notable structure of hexagonal columnar symmetry, each column is formed from a single polymer chain, but far from being of all-trans conformation as in the crystalline phase, the skeletal conformation in the mesophase appears to be practically entirely in an all-gauche helical conformation; this change of phase from the crystal is thus accompanied by a significant alteration of the intramolecular conformation. In general it is clear that the synthesis and testing of polymers exhibiting desirable properties of orientation and response to electric and magnetic fields in the range of temperatures near ambient remains a worthy objective of chemical and physical research. One can also safely predict that probably mixtures of substances, each component contributing some set of desirable properties, offer greater flexibility in technological applications than single, pure compounds.

Finally we mention aspects of mesophases that are still in course of initial investigation. Although some salts (or ionic compounds) are known to exhibit liquid-crystalline properties, in both thermotropic and lyotropic conditions, no ionic compounds are found among the conventional plastic crystals. So far, few mesomorphic states of ionic mesogens are known, with a notable exception[40], to conduct electric current, but in the extant applications the utility of liquid crystals has depended more commonly on their electrically insulating properties. Polymeric ferroelectric liquid crystals have also been developed[41]. The development of compounds with peculiar magnetic properties is likely also to be useful. Paramagnetic nematic, smectic and discotic mesophases are already known[6], of which copper complexes are particularly notable. The possibility of both antiferromagnetic and ferromagnetic interactions has already been recognised[6,40], and the technological exploitation of such properties will doubtless ensue. Whereas some uncomplexed Schiff bases, containing a -CH = N- group such as in compounds (19) and (20) for instance, have only nematic mesophases, some copper complexes containing these ligands show only smectic mesophases (smectic C, B and A phases in one particular case[40] in the order of increasing temperature in the range 363-413 K); thus the incorporation of a metal atom between two organic mesogenic ligands leads to more ordered mesophases. It is clear that the synthesis and characterisation of new mesogenic compounds leaves as much scope to inorganic and organometallic chemists as to organic chemists, just as the measurements of the electrical and magnetic properties present many opportunities for useful research by physical chemists and physicists. Mesophases and mesogens will continue to be a fertile area of research across many fields of chemical and physical science.

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