polymer review

Properties of polymer liquid crystals: choosing molecular structures and blending

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Monomer liquid crystals (MLCs), polymer liquid crystals (PLCs) and heterogeneous composites are
compared. PLCs are classified into categories in function of their molecular structure. Molecular composites
(MC) are characterized. Phase diagrams are analysed, and new ways of presenting information on coexisting
phases including glassy ones are proposed. Rheology and methods of processing of PLCs and MCs are
outlined. Characterization of PLCs including their dielectric behaviour is discussed. Blending of PLCs and
properties of the blends of MCs are related to present as well as potential applications of liquid-crystalline
and rigid rod materials.

MONOMER AND POLYMER LIQUID CRYSTALS

Liquid crystals have been known for more than a full
century. Just as all organic compounds, liquid crystals
can be divided into two categories in function of their
molecular mass. Thus, we distinguish monomer liquid
crystals (MLCs), irrespective of the fact whether these
monomers can be polymerized, and polymer liquid
crystals (PLCs). This convenient terminology is due to
Samulski[1]. Some authors use an inverse name for PLCs,
that is liquid crystal polymers or LCPs. The main reason
for the current and certainly also future high level of
interest in PLCs lies in their properties. As discussed by
Witt[2], compared to widely used engineering thermo-
plastics, PLCs show clear superiority with regard to
chemical resistance, low flammability, high modulus, low
isobaric expansivity (or even zero, depending on the
direction) and often unusual ease of processing. Materials
in which liquid crystalline properties appear induced by
the presence of a solvent are called *lyotropic*; I shall not
consider them in this article in detail. I shall deal mostly
with *thermotropic* materials in which LC properties
appear in defined temperature T intervals. Hsiao, Shaw
and Samulski[3] found that liquid crystallinity can also be
brought about by pressure P elevation; by analogy, I
propose to call such LCs *barotropic*. Their existence is
not surprising, since pressure and temperature changes
produce similar (although not identical) effects in terms
of affecting free volume; recall for instance the tempera-
ture and pressure shift factor $a_{T,P}$ of Fillers and Tschoegl[4].
Moreover, I shall discuss molecular composites (MC)
which are related to LCs.

In spite of the respectable age of MLCs, their
applications are only a few decades old; some current
applications of PLCs are only a few years old. PLCs are
of interest for quite a few branches of industry. The key
question is: how to achieve desired mechanical, thermo-
physical, optical, rheological, electrical, magnetic and
other properties? There are at least two ways of reaching
properties one wishes: either by choosing appropriate
molecular structure or by blending. One can also
combine these two approaches. Therefore, in the present
review I shall compare PLCs with composite materials;
discuss phase structures of PLCs and other mesophases
and amplify a classification of PLC molecular structures
developed earlier[5]. Further, I shall discuss phase diagrams
of PLC-containing systems, proposing some new ways
of presenting information on kinds and amounts of
co-existing phases. Given this basis, I shall be able to
deal with processing of PLCs and MCs and with ways
of attaining desired properties in pure PLCs and their
blends.

PLCs, HETEROGENEOUS COMPOSITES AND MOLECULAR COMPOSITES

Central to liquid-crystalline properties is the anisotropy
of shape and interaction of molecules or their parts.
Because anisotropy is easily produced by molecular
rigidity, most LC compounds contain rigid parts. To
evaluate better effects of rigidity, consider now briefly
composite materials. As discussed in textbooks of materials
science and engineering (see e.g. Chapter 10 of ref. 6),
in fibre composites the components perform different
functions: rigid fibres carry load while a matrix distributes
load. Mechanical properties of the composite are much
better than those of either of its constituents. However,
given large differences in the nature of fibres and the
matrix, sufficient adhesion between the composite con-
stituents is often a problem; cases of fibre pullout and
delamination are well known. Problems of creep, fracture

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initiation and failure in fibre composites have been reviewed by Piggott[7] and by Jansson and Sundström[8].

Following a suggestion made in ref. 9, I shall use the name *heterogeneous composites* for the traditional composite materials. There are at least two good ways of eliminating problems inherent in their use. One is to use PLCs in which in most cases each chain already contains rigid and flexible sequences connected by primary chemical bonds. The other consists in the dispersion at the molecular level of rigid chain molecules in flexible chain materials, the concept of *molecular composites* developed by Helminiak, Hwang and collaborators[10,11].

In both MCs and PLCs the problems of adhesion of large rigid units to flexible ones are eliminated from the start. Their mechanical properties are at least as good as those of the heterogeneous composites[12], while their processing is easier. It would be an error, however, to conclude from the above that heterogeneous composites are due to disappear completely and to be replaced by MCs and PLCs. The latter have a share of problems of their own. Monomers for PLC synthesis are often available in small quantities only, and therefore the polymers have high prices. This is the reason for blending PLCs with ordinary engineering polymers. One hopes to preserve good properties of the PLC in the blend, but obtain the material at a much lower cost than pure PLC.

MESOPHASE STRUCTURES

Phases with microscopic structures between solids and ordinary isotropic liquids have been called mesomorphic by Friedel in 1922[13]. In 1955 Kast[14] tried to characterize them in terms of lateral, longitudinal and steric disorder. Now, following Wunderlich and Grebowicz[15], we distinguish three kinds of mesophases: LCs, plastic crystals and condis crystals.

To define differences between mesophase types, I have first to describe positional, orientational and conformational disordering. A convenient example for this is melting of the homologue series of *n*-paraffins. When methane melts, various relative positions of its quasi-spherical molecules become possible; the melting process is said to be accompanied by *positional* disordering. There is a respective contribution to the entropy of fusion. When ethane melts, we have similar positional disordering (less uniform intermolecular distances), but we also have *orientational* disordering: two ethane molecules can be parallel to each other, or perpendicular, or anything in between. A longer paraffin such as *n*-decane also undergoes on melting positional and orientational changes, but dominating in this case is *conformational* disordering, that is the acquisition of freedom of executing rotations about single bonds. As noted by Wunderlich and Grebowicz[15], camphor contains ten carbon atoms, equally as decane, but the camphor molecule is nearly spherical and rigid and there are no orientational nor conformational effects. Consequently, the entropy of fusion of camphor is much lower than that of *n*-decane.

Similarly as crystals, all three kinds of mesophases have some degree of long range order. Similarly as ordinary isotropic liquids, they also have some degree of mobility other than segment vibrations. Specifically: LCs exhibit positional disordering; *plastic crystals* show orientational disordering; and *condis crystals*, defined for the first time by Wunderlich and Grebowicz[15], show conformational disordering. Wunderlich and his col-

leagues[15-17] point out that condis crystals are sometimes mistaken for LCs. Each of these three phases can also form a corresponding glassy phase.

Let us now try to acquire a better idea of the nature of liquid crystallinity. Common to all LCs is the fact that the molecules are oriented approximately parallel to a preferred axis in space called *director*. The degree of alignment is defined by the so-called *order parameter* or *anisotropy factor s*:

$$s = 0.5(3\overline{\cos^2 \theta} - 1) \qquad (1)$$

Here θ is the angle between the molecular axis and the director, and the bar above denotes an average for the material. Thus, in a completely isotropic system $s = 0$ and in a perfectly aligned system $s = 1$. The presence of the director produces anisotropy of properties; for instance, refractive indices and dielectric constants become tensors instead of scalars. In an isotropic liquid, if, for example, an electrical or magnetic field is applied, the effects are small. The molecules respond individually. The energy difference between the alignments of a molecule parallel or perpendicular to the field is much less than the thermal energy represented by kT (k = Boltzmann's constant). By contrast, if we apply an equal field, even a weak one, to an LC, the effects are much larger. Just as ordinary solid crystals, LCs exhibit collective behaviour. The existing orientation is easily reinforced because the orienting effects of the field are, in the first approximation, proportional to volume of a collectively responding unit.

If orientation along a director is the only kind of long range order present, we have a *nematic* LC. A pile of nematic layers with the director changing from one layer to another forms a *cholesteric* phase. There are a number of *smectic* phases, with layer structures, and some of them with additional long-range order within each layer. Thus, each such phase has, in addition to the director, at least one more element of a long-range order. For instance, in each smectic A phase the molecular centres lie on equidistant planes perpendicular to the director. In smectic B phases we also have such planes, but additionally there is a two-dimensional hexagonal lattice within each plane. In smectic C phases there is no hexagonal structure, and the director is tilted with respect to the plane normal; the latter property distinguishes the phase C from A. Schematic representations of a nematic, a cholesteric and one smectic—namely C—phase are shown in *Figure 1*. A more detailed discussion of phases that can be formed in liquid crystals is given in Chapter 6 of reference 6. Each kind of LC phase such as nematic can appear in MLCs as well as in PLCs.

As discussed by Sackmann[18], a solid upon melting sometimes produces first a more complex LC phase, for instance a smectic one. After a further temperature
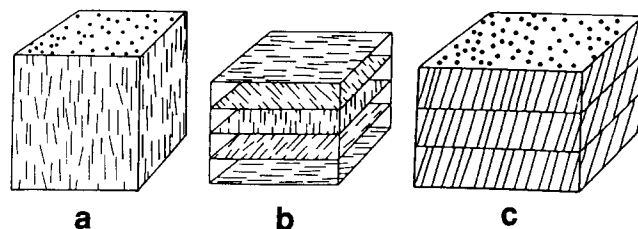

a   **b**   **c**

Figure 1 A schematic representation of (a) a nematic, (b) a cholesteric and (c) a smectic C phase

increase a simpler such phase, such as smectic A and/or nematic appears. Eventually at the clearing temperature the liquid becomes isotropic. MLC compounds, the kinds of phases they form and the respective transition temperatures are listed in books by Demus, Demus and Zaschke[19,20].

An interesting phenomenon was discovered by Limmer, Schmiedel, Hillner and Lösche[21]. In LCs which produce low-temperature smectic phases (for instance smectic G, with vertical herringbone symmetry), when a high-temperature phase (smectic A) is aligned in a magnetic field, cooled down until it solidifies and reheated again to the original temperature, the alignment is still present. Apparently, the material in the solid phase 'remembers' for weeks, and presumably much longer, what happened to it when it was still a liquid.

Nematic phases align more easily than smectic ones. An ingenious method of aligning the latter was developed by Patel and collaborators[22]. A ceramic is covered with a layer of one of several ordinary polymers (polyethylene, nylon), rubbed unidirectionally, and then covered with a smectic LC.

LC phases have spectacular and often colourful textures which are illustrated in a book by Demus and Richter[23]. Given changes in textures and colours of cholesteric LCs at specific phase transition temperatures, one of the applications of MLCs is in the field of visual temperature sensors, already in use in medicine and applicable also in the automobile industry.

The reason for the appearance of the director in MLCs is, of course, the rigidity of the molecules present. PLCs are typically copolymers containing rigid LC sequences intercalated with flexible ones (completely rigid chains are made also, but one usually wants to lower the melting point). Therefore, rigidity in typical PLCs is weaker in comparison with MLCs. For reasons discussed following equation (1), it is easy to strengthen the alignment of rigid sequences and thus to increase the anisotropy in a PLC material. Typically, anisotropy can be enhanced by melt processing, and this even at relatively low shear rates; also by imposition of an electric field, a magnetic field[24], drawing[25] or stretching[26].

Soft (S) and rigid (R) LC sequences might alternate, as might do two types of sequences in an usual non-LC random copolymer. In the extreme case of a perfectly ordered structure, the snake (that is a chain without branches) would have the arrangement ...SRSRSRSR... Deviations from this structure occur, however. One of the best known PLCs is a copolymer of poly(ethylene terephthalate) (PET) with p-(acetoxybenzoic acid) (PHB) obtained and studied first by Jackson and Kuhfuss[27]; we shall denote it by PET/xPHB, where x is the mole fraction of the modifying LC component. Nicely and collaborators[28] studied systems containing such copolymers, varying value of x, in solution and as melts by n.m.r. spectroscopy. They have found that there is a preference factor of 1.3 for two LC groups being adjacent to each other, that is for the ...RR... structure in comparison to a random distribution of S and R units.

CLASSIFICATION OF PLCs

Liquid crystal molecules can be constructed from a variety of structural elements. Anatomy of MLCs from this point of view was surveyed in detail by Demus[29,30].

As for PLCs, one usually characterizes their molecular structures from the point of view of location of R sequences. Thus one talks about main-chain PLCs in contrast to side-chain copolymers; the latter are also called comb liquid crystals. However, there are more possibilities than just these two. Several of them were listed by Krone, Reck and Ringsdorf[31]. The first comprehensive classification scheme that enables a precise definition of a kind of PLC one is dealing with was proposed in reference 5. Since then synthetic chemists have added to the variety of PLC classes. Latin letters designating classes in the original classification[5] have now been replaced by Greek ones (this to avoid confusion with smectic phases, traditionally denoted by capital Latin letters). The scheme amplified accordingly is provided in *Table 1*. New names proposed as part of this classification are italicized. Differences in molecular structures cause large differences in properties. I now discuss in some detail each of the classes.

Class α, longitudinal LC polymers, called earlier main-chain polymers

A new name is necessary to distinguish them from the following classes β and γ and the subclasses ζS, ζR and λ1. There are numerous examples of class α, including the already mentioned copolyester PET/xPHB of Jackson and Kuhfuss, Vectra manufactured by Hoechst-Celanese and Xydar manufactured by Dart. Lenz and collaborators[32] studied longitudinal polyesters in which the rigid LC groups are connected together by either rigid or flexible non-LC spacers. Their objective is to delineate the relationships between the molecular structure and properties, the types of phases formed in particular. There are also polyesters with azo and azoxy groups[33,34], including a series of azoxybenzene polyesters studied systematically by Blumstein and Blumstein[35]. Kricheldorf and collaborators[36-38] conduct extensive studies of synthesis and properties of poly(ester imides) as well as of polyesters[39,40]. Further, poly(ester amides)[41] and polyurethanes[42] also form longitudinal structures.

Class β, orthogonal LC polymers

As class α, they also contain LC groups in the main chain, but now these groups are approximately perpendicular to the backbone. Two kinds of such polymers were obtained in the Ringsdorf laboratory[31], namely based on the siloxane chain
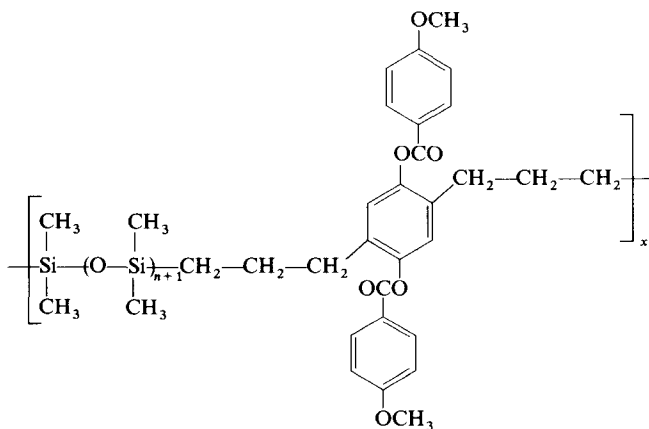

where n varies between zero and five, as well as polyesters

Table 1 Classification of polymer liquid crystals on the basis of molecular structures. Figures other than wavy lines (rectangles, circles, etc.) represent LC elements

| Class	Structure	Name English	German
α		*longitudinal*	*longitudinal*
β		*orthogonal*	*orthogonal*
γ		*star (cross)*	*Stern (Kreuz)*
ζS		*soft disc*	*biegsomer Diskus*
ζR		*rigid disc*	*steifer Diskus*
ζM		*multiple disc*	*Multidiskus*
εO		*one-comb*	*Einzelkamm*
εP		*palisade-comb*	*Palisaden-kamm*
εD		*double comb*	*Doppelkamm*
ψ		*disc comb*	*Kammdiskus*
κ		*inverse comb*	*invertierter Kamm*
θ1		*parallel*	*parallel*
θ2		*biparallel*	*biparallel*
λ1		*mixed*	*gemischt*
λ2			
λ3			
ψ1		*double*	*doppelt*
ψ2			
σ		*network*	*Netzwerk*
ω		*conic*	*Kegelförmig*

of the type
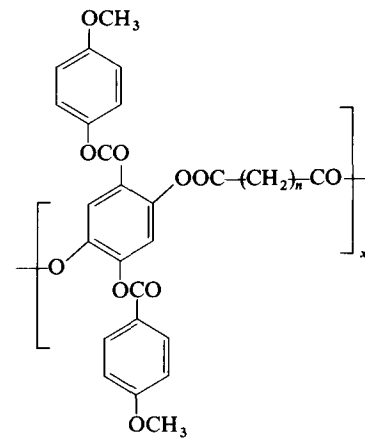
In this second series it appears that crystalline and LC regions coexist until the clearing temperature.

Class γ, star PLCs

Four-member stars, that is crosses, were synthesized for the first time by Krone, Reck and Ringsdorf[31], leading to structures
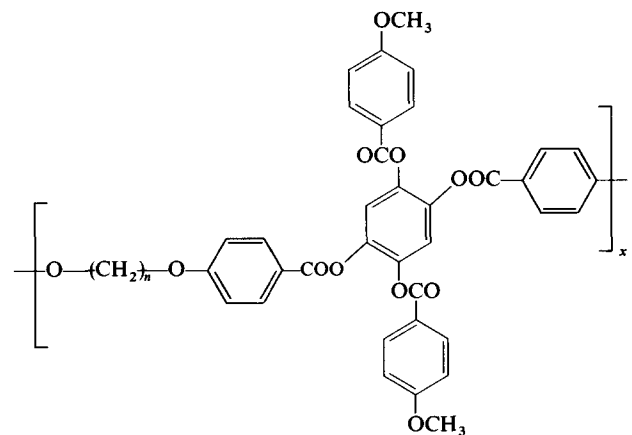
In distinction to polyesters in Class β which are monotropic, polymers in Class γ are enantiotropic.

Class ζ, discotic polymers

Here a variety of molecules were already synthesized, including polysiloxanes, polyamides and polyesters. These materials exhibit low molecular mobility. Two subclasses were distinguished in the original classification[5], but now we recognize three.

(1) Subclass ζS, with single discs in the main chain and soft spacers between them. Two packing structures possible here and expected to coexist with each other were proposed by Wenz[43] and are shown in *Figure 2*.
(2) Subclass ζR, also with single discs in the main chain
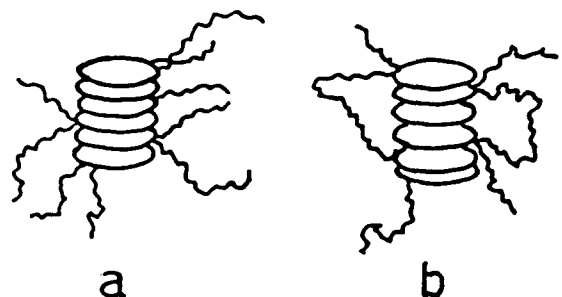
Figure 2 Packing of DS (discotic soft) polymers (after Wenz[43]): (a) ties leading to other stacks; (b) spacers within a stack
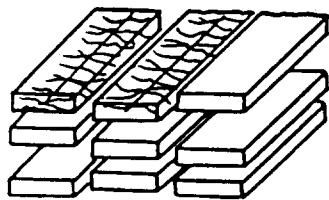
Figure 3 Packing of DR (discotic rigid) polymers (after refs 44 and 45)

but with rigid spacers. Wendorff, Ringsdorf and collaborators[44,45] have proposed a sanidic (from the Greek for board-like) packing structure which is shown in *Figure 3*.
(3) Subclass ζM, with a multiple disc in the centre. Following an attempt by Lattermann and Höcker[46], Latterman[47] has obtained two examples of this subclass. There is a central core, either a benzene or a cyclohexane ring, connected via ester groups to three further cores, and on each of the latter there are three decyloxy-chains in positions 3, 4 and 5.

Class ε, combs or ε-shaped structures

These structures were developed by Shibaev and Platé[48] and independently by Finkelmann, Ringsdorf and Wendorff[49] by the introduction of a flexible spacer between the backbone and the LC segment. Subsequently, Zhou, Zhu and Wen[50] have shown that the flexible spacer is not necessary. It is possible to distinguish between three subclasses, based on the function of the arrangement of the side chains.

(1) Subclass εO, combs with one row of side chains. A fairly large variety belongs here, including azo[51], azoxy[52] and phenylazo-azobenzene[53] LC polymers. Group-transfer polymerization developed by Webster[54], which allows good control of the molecular mass, was used to obtain LC polymethacrylates[55]. In most cases the flexible spacer consists of methylene groups connected to the mesogenic moiety via an ether linkage. However, de Marignan and his colleagues have obtained molecules with a carbonate instead of ether[56].
(2) Subclass εP, combs with a palisade of side chains[57]. Thus, a line drawn through the gravity centres of the LC groups has the shape of a zigzag.
(3) Subclass εD, with double or paired mesogens. A number of polymers with polysiloxane backbone were obtained[58-61].

Class φ, disc-comb structures

Such polymers were synthesized by Kreuder and Ringsdorf[62], with triphenylene derivatives as the discs.

Class κ, inverse combs, with rigid backbones and flexible side chains

Nematic LCs were obtained by Weissflog and Demus[63,64] with fairly short backbones. Polymers with higher molecular masses were synthesized by Ballauf[65,66].

Class θ, parallel structures

In these structures, the LC groups are in side chains and oriented approximately along the chain backbone. One can distinguish here two subclasses, depending on the location of the mesogenic groups with respect to the backbone, because apparently conformational transitions are difficult.

(1) Sublcass θ1, or simple parallel. Such polymers were obtained first by Hessel and Finkelmann[67], later by Zhou and collaborators[68], and also by Keller, Hardouin, Mauzac and Achard[69]. Elongation of a flexible spacer can produce a biparallel (the following subclasses) molecule instead of parallel. Moreover, parallel–biparallel conversion apparently can occur for a given molecular structure by varying temperature[69].
(2) Subclass θ2, biparallel structures. This class, with nematic structures, was obtained in the Finkelmann laboratory[70] and called biaxial. However, the word biaxial is also used in connection with studies of structures of smectic C phases[71,72]. A low molecular mass θ2 compound was synthesized by Malthete and his colleagues[73]. A polysiloxane with phenyl benzoate mesogens obtained by Finkelmann was studied by Hotz and Strobl[74].

Class λ, mixed structures

In these, nematogens of different shape or orientations occur together. Several possibilities exist here. These include the following.

(1) Subclass λ1, in which mesogens are alternating between parallel and perpendicular positions with respect to the backbone. Such PLCs were obtained by Weissflog, Kuschel and collaborators[75].
(2) Subclass λ2, with disc-shaped and rectangular mesogens alternating along the backbone, with the latter aligned with the backbone.
(3) Subclass λ3, similar to class λ2 but with the rectangular mesogens perpendicular to the backbone direction.

Class ψ, double or combined PLCs

These have LC groups in the main chain and in branches. First synthesized were polyesters by Reck and Ringsdorf[76]. Two subclasses are possible, in function of the location of side groups with respect to the backbone:

(1) Subclass ψ1, with the spacers attached to the flexible sections of the main chain.
(2) Subclass ψ2, with the spacers attached to the mesogens in the main chain.

Class σ, PLC networks

These have elastomeric properties, and were obtained first by Finkelmann, Kock and Rehage[77] in 1981. More such materials were since made by Finkelmann[78], Davis and Mitchell[79], Zentel et al.[80,81] and Jones et al.[82,83]. It should be noted that elastomers have been made from longitudinal (class α), one-comb (subclass εO) as well as double (Class ψ) molecules. In *Table 1* under Class σ I show as an example an elastomer made from comb chains.

Class ω, conic molecules

Classes α–ψ could be planar, or nearly two-dimensional. Networks are typically three-dimensional, but a planar class σ molecule is possible, at least in principle. By contrast, molecules in Class ω must be three-dimensional. Their existence was predicted by Lin[84] in 1982 but confirmed experimentally several years later[85,86]. Names pyramidic or bowlic were proposed, but I eventually decided to adopt the name conic. Lin predicts[87]

that these materials should have interesting electric properties.

Related to molecular structure and to properties is the problem of packing of PLC chains. We have already shown two ways of packing of ζS discs in *Figure 2*. I have further shown sanidic packing of ζR discs in *Figure 3*. One also talks about calamitic phases made of elongated molecules, apparently contrasting them with disc structures. Packing intermediate between the usual nematic (which is calamitic) and sanidic is also possible[88]. Destrade and his colleagues[89] developed terminology for packing structures: bacillar = finite cylinder, lenticular = disc, lamellar = infinite sheet and columnar = infinite cylinder. Bacillar packing is expected in nematic phases while lamellar in smectic (other than smectic D) phases.

I have already noted the problem of regularity of constituting elements in PLC chains, such as the regular structure ...SRSRSR.... Stupp and collaborators[90-92] studied the problem of regularity, or lack of it, experimentally as well as by computer generation of irregular chains containing three kinds of units. Stupp introduces[92] a concept of polyflexibility, which implies a distribution of persistence lengths. As expected, polyflexibility does affect properties, including the sharpness of the nematic-to-isotropic transition.

While so many classes of PLCs exist, we still do not know exactly what causes liquid crystallinity. To arrive at this understanding, Aharoni[93] studied some 90 poly-(ester amides) (PEA). He concluded that mesomorphicity appears to be limited to highly regular, strictly alternating aromatic-aliphatic PEAs in which the methylene sequences are neither too short nor too long and where interchain hydrogen bonds hold the structure together. Weissflog and Demus[94] synthesized 2-substituted hydroquinone bisbenzoates with large 2-substituents containing aromatic and other ring systems. Contrary to a widely held opinion, the large substituents did cause considerable deviations from the rod-like shape of the molecules, but did not prevent liquid crystallinity. Nematic and smectic phases are formed. Thus, prediction of liquid crystallinity remains an open question.

A HISTORICAL PERSPECTIVE

Given the current explosion of research and applications of LCs, many laymen, and even some researchers, do not realize how long these materials have been with us. Liquid crystals were discovered by the Austrian botanist Reinitzer more than one hundred years ago[95]. Lehmann, who before Reinitzer talked about 'plastic crystals' and recognized the importance of polarizing microscopy[96], is credited with introducing after Reinitzer's discovery the name 'liquid crystals'[97]. Since the beginning of the twentieth century Vorländer synthesized many LCs and studied their properties[98]. This work is still carried on at Martin Luther University of Halle-Wittenberg today, now by Sackmann, Demus and Kuschel. After more than two decades of working on MLCs, in 1923 Vorländer realized that PLCs must also exist. In his words[99]: 'What happens to the molecules when one makes them longer and longer? Will the liquid crystalline state disappear? From my experience there is no limit to that state by chain elongation, unless the substances could not melt any more without decomposition and could not be seen under a microscope. Starting from the *p*-oxybenzoic acid, Klepl[100] and later Emil Fischer and his colleagues[101]

obtained long chains, but did not realize their liquid crystalline character'. Hermann Fischer gave some samples prepared by his father Emil to Vorländer, and the latter found that they were liquid crystalline[99]. Thus, German researchers had worked with polymer liquid crystals in the nineteenth century.

THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND PROPERTIES

I shall provide just one example to illustrate that the molecular structures of PLCs determine their properties. For longitudinal polymers typically the viscosity in the isotropic phase is higher than in the nematic phase. Thus, lowering the temperature so as to get below the clearing point produces a viscosity decrease. Apparently a partial alignment occurs during shear flow of the nematic, a phenomenon similar to the domain formation by drag reducers in solution flow[102]. For LC melts, however, this is not a general phenomenon. Zentel and Wu[103] studied melt flows of one-row combs, that is subclass εO. They have found a negligible dependence of viscosities on shear rates for isotropic and nematic phases. Moreover, in contrast to longitudinal LCs, viscosities in nematic phases were higher than in isotropic ones. Apparently the alignment of mesogenic side groups had, because of their flexible connections to the backbones, too little influence on flow of the entire chains.

MOLECULAR COMPOSITES

MCs are in many ways similar to PLCs. In a typical PLC there are rigid and flexible sequences within each chain. As developed by Helminiak, Hwang and colleagues[10,11], in a MC completely rigid chains are dispersed so well with flexible ones that a similar result is achieved. Strictly speaking, many rigid chains and thus rigid rod constituents in MCs are liquid crystalline, but I consider them separately from PLCs to follow the established usage, and also because molecular rigidity by itself does not by itself automatically bring about liquid crystallinity. Nor is it true that LCs must be rigid, because relatively flexible molecules of *n*-alkane-1,2-diols form thermotropic LCs[104].

With the reinforcement by rigid constituents, in both MCs and PLCs good mechanical properties are achieved. A quantum-mechanical molecular-orbital study of Wierschke[105] shows how outstanding tensile and compressive properties can be attained for individual rigid rods. Moreover, a study by Denny, Goldfarb and Soloski[106] shows how MCs also distinguish themselves by very good thermal stability. Still further, as reviewed by Ulrich[107], MCs have applications based on their non-linear optical properties. As noted by Adams and Eby[108], the fibre-based materials are of particular interest to the aerospace industry; this because of high stiffness, low density in comparison to traditional materials, and capability to be used for making mission-adaptive wings, that is wings with shapes which can be changed during a flight. One more advantage of MCs, or organic materials in general, for military applications is the radar invisibility (stealth).

With all the advantages, high rigidity of MC materials presents special processing problems. These problems can be overcome, however[10]; a special volume on preparation, processing and properties of rigid-rod polymers has been published[109].

HIERARCHICAL APPROACH TO MORPHOLOGY OF PLCs AND MCs

Propensity of rigid sequences to orientation during processing results in fibrillar morphologies of PLCs and their blends in the solid state. Thus, the resulting structures must be considered at several levels. A hierarchical scheme providing a convenient approach to dealing with this problem has been proposed by Sawyer and Yaffe[110]. The scheme, which is practically self-explanatory, is shown in *Figure 4*.

PHASE DIAGRAMS

To achieve desired structures and properties of PLC or MC materials, it is necessary to take into account: molecular structures, morphology, phase equilibria, and rheology and processing. I will now go on to discuss phase equilibria.

Multiphasicity seems to be a persistent feature of mesophase materials. Just as in ordinary polymers, we cannot limit ourselves to equilibrium diagrams *sensu stricto*, as this would eliminate glasses and other non-equilibrium but long-living phases. Thus, in all phase diagrams considered below non-equilibrium phases are taken into account. I consider pure PLCs first, then binary systems: MLC + MLC; MLC + PLC; PLC +

a non-mesogenic low-M compound; PLC + a non-mesogenic polymer; and finally, ternary systems.

Even pure mesogenic polymers exhibit very interesting phase behaviour. In simple combs (subclass εO) a number of LC phases was found by Freidzon and his colleagues[111]. PET/xPHB copolymers, studied by Menczel and Wunderlich[112-114] by differential scanning calorimetry (d.s.c.) were found to form two solid phases, each with its own glass transition. This seems to be a typical phenomenon for PLCs. On the basis of a number of techniques including scanning electron microscopy (SEM) of fracture surfaces and wide angle X-ray scattering (WAXS), Brostow and his colleagues[115] have constructed a structural model for the mesophase-rich *islands*. The name islands for such regions was proposed in reference 9. It is a hierarchical model, as shown in *Figure 5*.

First, the LC sequences come together and form an island (*Figure 5a*). However, they necessarily drag with them flexible sequences to which they are connected. Then, LC sequences align and crystallites are formed, such as the one shown in *Figure 5b*. The flexible connectors stay outside, that is between the crystallites, but inside the islands.

Lin and Winter[116] studied a longitudinal PLC, Vectra A900 (Hoechst-Celanese) containing 73 mol% PHB and the rest 6-hydroxy-2-naphthoic acid (HNA). Above the melting point of 280°C, the nematic shows a modulus increase by three orders of magnitude in 200 min, and a high-melting crystal is formed. Heating to 320°C destroys the crystals and even their nuclei. Afterwards no significant crystallization from the nematic occurs in 290°C.

Hotz and Strobl[74] found in their biparallel (subclass θ2) PLC that layers are the dominating structure element not only in the crystalline and smectic phase, but also in the nematic phase and even in the isotropic melt. Apparently in the isotropic liquid formation of clusters with layer-like short-range structures takes place.

I have already mentioned the possibility of parallel–biparallel conversion upon temperature increase presumed for a MLC[73] as well as for a PLC[69]. Blumstein and Blumstein[35] reported formation of a nematic-isotropic biphase for longitudinal azoxybenzene polyesters with regularly alternating mesogen moieties and flexible groups. Molecular segregation by chain length occurs in the biphase.

I now go on to binary systems, beginning with MLC pairs. Important studies for these were performed by Arnold and Sackmann in 1960[117,118]. They established that complete miscibility of LCs is always connected with isomorphism. This is not a necessary but a sufficient condition. Thus, if a nematic phase is miscible with a second phase, that second phase is also nematic; a smectic phase of a given kind mixes with a like smectic one, while a nematic LC does not mix with any smectic. Several decades later, Sackmann[18] reviewed studies confirming this rule, including a binary system in which five smectic phases and a nematic phase are formed.

I noted earlier that lowering the temperature produces typically a more complex LC phase. However, reentrant nematic phases (RN), existing at temperatures below smectic phases, are also possible[119]. Sackmann, Demus and collaborators[120] studied binary MLC + MLC systems forming RN phases. While it was presumed before that such phases can be formed in unary and binary systems of strongly polar compounds only, their compounds contain terminal non-polar groups. In some cases Sackmann
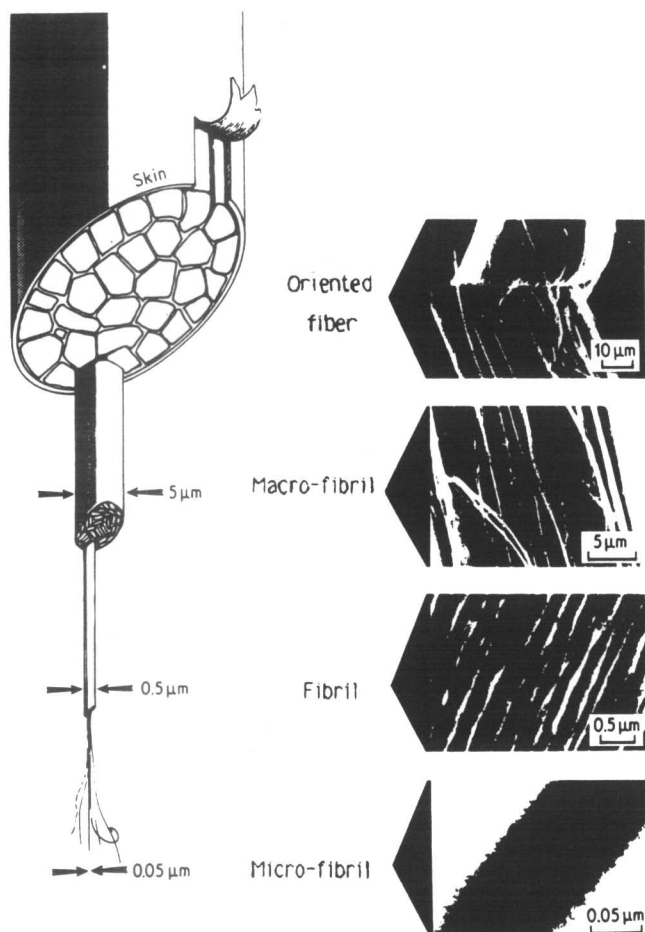

Figure 4 A hierarchical model of PLC morphology according to Sawyer and Yaffe[110]: left, schematic; right, micrography of oriented materials

Island
Diameter between 1.0 and 1.4 μm. Small unfilled regions inside with approximately spherical shapes represent LC-crystallites. Lines between the crystallites represent some of the flexible sequences in chains

LC-crystallite
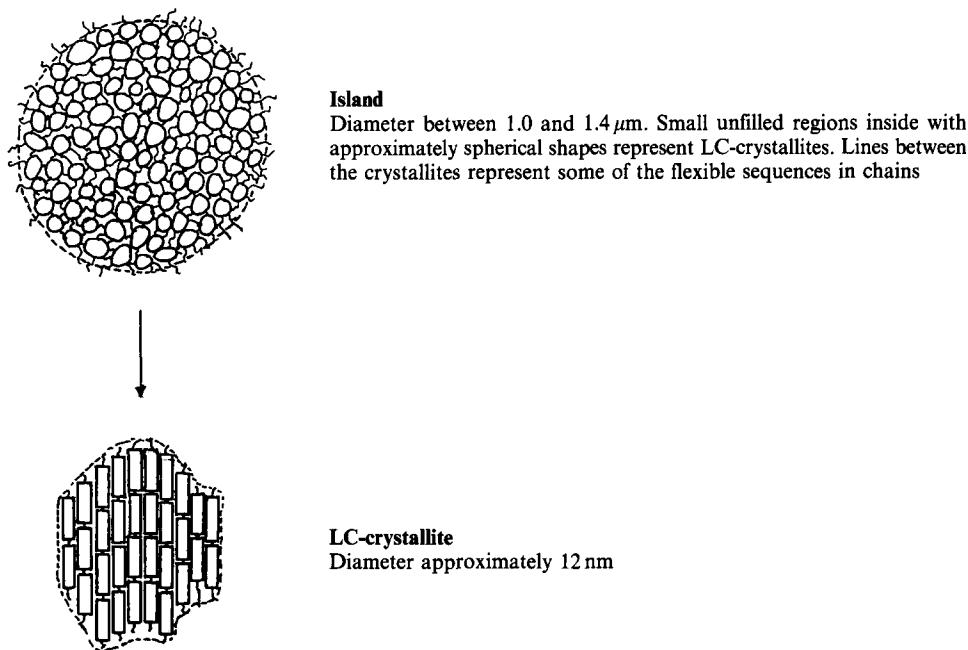Diameter approximately 12 nm

Figure 5 A hierarchical model of LC-rich islands according to ref. 115

et al.[120] found a smectic A phase in the middle of a phase diagram, while pure components themselves form no such phases.

The Arnold–Sackmann rule was sometimes misunderstood as a necessary rather than a sufficient condition; that is, one assumed that two identical phases such as nematic must be miscible. In 1982 Casagrande, Veyssié and Finkelmann[121] found that a nematic MLC mixed with a nematic εO-subclass PLC exhibit a miscibility gap; this is in spite of large similarity of mesogenic groups in both compounds. Similar results were obtained for another such pair by Benthack-Thoms and Finkelmann[122]. Many more diagrams of MLC + PLC pairs were studied, notably by Sigaud, Hardouin and their colleagues in Bordeaux and Saclay[123,124]. They found that stiffer MLCs mix better with PLCs. Alexandre Blumstein and collaborators[125] studied a MLC, namely *p*-heptyloxyazoxybenzene (PHAB) mixed in turn with two PLC polyesters differing only in M. PHAB forms a smectic phase; in mixtures with PLCs the smectic region in the phase diagram was much smaller for a PLC with $M = 4 \times 10^3$ than for the other polymer with $M = 3.0 \times 10^4$.

Quantitative treatment of MLC + PLC systems is also possible. George and Porter[126] have taken bis(*p*-(methoxycarbonyl)-phenyl) terephthalate (DMELC) which is a MLC and mixed it with PET/*x*PHB with $x = 0.8$. According to a thermodynamic theory for melting point depression adapted to polymeric (originally non-LC) systems by Flory[127]

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(V_u/V_1)(\phi_1 - \chi_1\phi_1^2) \qquad (2)$$

where T_m is the melting point of the mixture, T_m^0 the melting point of the pure main component (100% crystalline polymer in this case), R the gas constant, ΔH_u the enthalpy of transition per mole of polymer repeat units, V_u the molar volume of polymer repeat units, V_1 the molar volume of the other component (solvent, diluent, impurity), ϕ_1 the volume fraction of the same component and χ_1 the Flory interaction parameter. George and Porter have shown that equation (2) is also applicable to PET/0.8 PHB diluted with DMELC. There is no question that their generalization of that equation can be used for any systems with a PLC as the major component. They even tried the use of equation (2) for PHB diluted internally with PET, that is in a series of PET/*x*PHB with varying *x*, using the data from reference 114. Here the equation appears to be obeyed only approximately; more studies of this particular extension of the Flory equation seem worthwhile.

Kuschel, Rühlmann, Ringsdorf and collaborators[61] studied a polysiloxane double comb, subclass εD, mixed with a MLC of similar chemical nature. Somewhat unexpectedly, internal (molecular) dilution of the PLC by adding more siloxane segments between side-group carrying backbone segments improves miscibility; MLC becomes incorporated into smectic layers. They also studied their PLCs mixed with a low-molecular mass non-LC siloxane compound. The undiluted PLC, that is with the double mesogen at each backbone segment, was totally immiscible with the compound. However, diluted PLC, more chemically similar to the compound, is miscible in both its isotropic and smectic A phases with the compound. This is in contrast with earlier experience that LC properties disappear if only a few mol% of an isotropic phase are added to a smectic one.

I now go on to binary PLC + polymer systems in which the latter does not contain mesogenic groups. Only a few such systems have been studied. Zachmann and collaborators[128] studied poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) blended with PEN/*x*PHB copolyesters. They have obtained a phase diagram which shows two PHB phases. The diagram is instructive because of its complexity. At the same it is not complex enough; contradicting experimental findings in the same paper such as a stable biphasic LC + isotropic region of vertical height of some 30 K, the diagram shows one-phase regions only.

A fairly complex phase diagram has been found for PET/0.6 PHB blends with poly(bisphenol-A-carbonate) (PC)[128]. Taking into account glassy phases, it contains
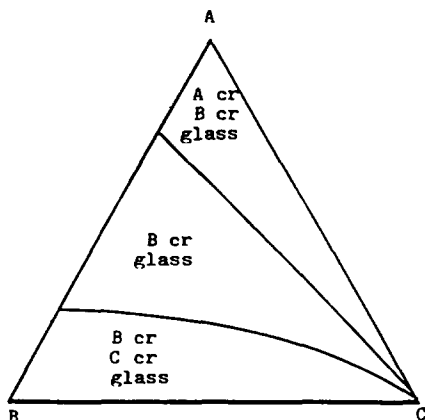
Figure 6 A binary $A + BC$ system treated as ternary (a hypothetical diagram for T=constans). In this example B is the liquid crystalline component in BC copolymer
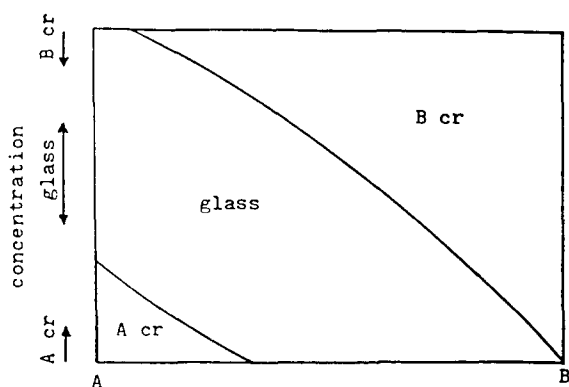
Figure 7 Diagram for a binary $A + B$ system showing the amounts of crystalline as well as glassy phases (a hypothetical diagram for T=constans)

a number of multiphase regions. To deal better in the future with defining and analysing information on coexisting phases, it is proposed to represent such information at isothermal conditions as shown in *Figures 6* and *7*. In *Figure 6* a hypothetical binary A + BC system is treated as ternary. Here B is the liquid–crystalline component in the BC copolymer. As drawn, the concentration variable along the base line going from left to right is, for instance, $1 - x$ in the PET/xPHB copolymer mentioned before.

A second suggestion, shown in *Figure 7* also as a hypothetical diagram, applies not only to liquid–crystal containing systems, but to any binary or quasi-binary system. It is customary to state numerically degrees of crystallinity of pure polymers. If components A and B in *Figure 7* represent such polymers, we can see changes of degree of crystallinity of each component with composition. We note that there is no reason for the lines in *Figures 6* and *7* showing these changes to be straight lines. (If I made a similar isothermal plot to that in *Figure 7* for a binary liquid system with a miscibility gap in the middle, the central part of the diagram would contain a straight line, corresponding to calculations that can be made with a lever rule; for miscibility gaps and the use of that rule see for instance reference 6.) In polymer systems, and those containing PLCs in particular, deviations from straight lines and from symmetry of the diagrams are expected in general[115,129]. For instance, Zachmann *et al.*[128] find that the formation of poly-PHB

crystals is much more hindered by the presence of, say, 10 mol% PEN than the formation of PEN crystals is hindered by the presence of 10% PHB. It is hoped that the diagrammatical representation proposed here will be useful not only for dealing with phase diagrams, but also with consequences of these diagrams for optimizing processing conditions and thus properties.

Finally, I consider ternary systems. Our understanding of phase equilibria in them is based largely on a statistical–mechanical theory developed by Flory and collaborators, first for a binary system of monodispersed rod-like solutes in a low-M solvent[130], then for binary systems of semi-rigid molecules in a solvent[131], for rigid rods with flexible side chains in a solvent[132], and further extended to ternary systems: two rigid rod-like solutes having unequal axis ratios and a solvent[133] and a rigid rod solute plus a randomly coiled flexible chain plus a solvent[134]. Separability of the partition function into intermolecular and intramolecular factors is assumed. The rod-like molecule is replaced by a succession of 'submolecules', with each submolecule parallel to the axis of the domain (see *Figure 8*).

A theory of Maier and Saupe[135,136] takes into account added stability of the nematic state due to the anisotropy of the dispersion forces. The Flory theory covers this as well, but it also takes into account two further factors: anisotropy of molecular shape, and the influence of that anisotropy on molecular packing.

For the ternary system of two rigid rods in a solvent[133] one finds that the miscibility gap is widened by mixing either solute component with the other; the isothermal diagram is highly asymmetric with respect to the two solute components. For the system solvent (1) + rigid rod (2) + flexible chain (3) Flory finds[134] that addition of 3 to the binary 1 + 2 system increases the volume fraction of 2 in the anisotropic phase and broadens the biphasic gap. Although glassy phases necessarily are not covered by equilibrium statistical mechanics, the Flory theory provides important guidance for dealing with PLC and MC systems.

RHEOLOGICAL PROPERTIES

Compared to non-LC polymers, PLCs (not only thermotropic polymers reviewed in this article but also lyotropic polymers) exhibit unusual rheological properties. Jackson and Kuhfuss[27] studied melt viscosities of their PET/xPHB copolymers in function of x and of the shear rate. Their results are presented schematically in *Figure 9*. After passing through a maximum at $x = 0.3$, viscosity goes
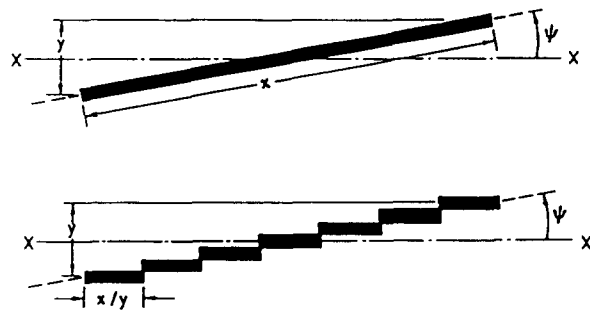
Figure 8 Representation of a rod-like molecule as a succession of y sub-molecules according to Flory for the purposes of statistical–mechanical analysis

down; then it goes up again when the concentration of the rigid component becomes too high. Equally interesting and even more useful is shear-sensitiveness: at high shear rates the viscosity of the copolymer is several orders of magnitude lower than that of pure PET.
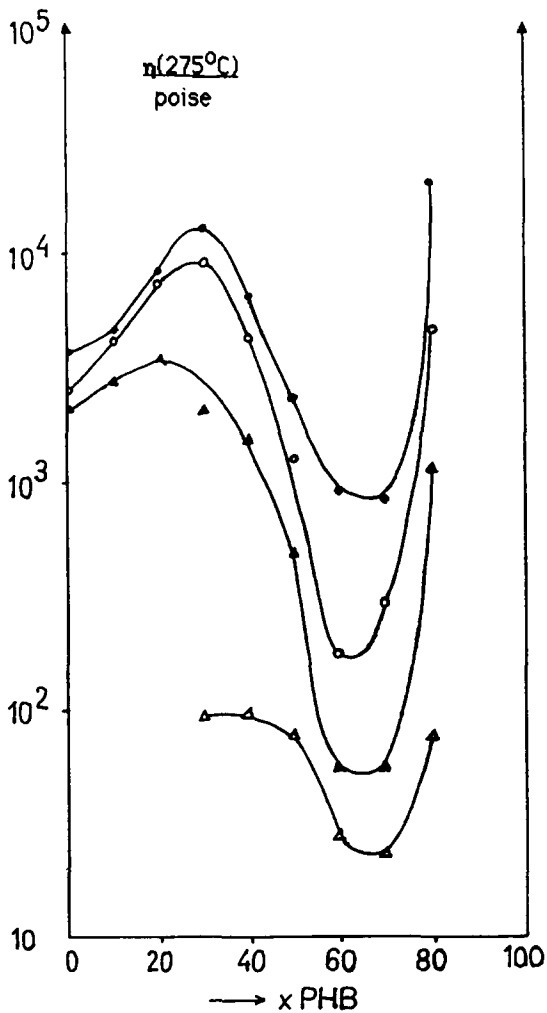

Figure 9 Viscosity of PET/xPHB melts at 275°C in function of x and of shear rate (after Jackson and Kuhfuss[27]). ●, $15 s^{-1}$; ○, $100 s^{-1}$; ▲, $1600 s^{-1}$; △, $54000 s^{-1}$

Extensive studies of PLC rheology were conducted by Wissbrun and collaborators[137-140]. They note that, compared to isotropic PLCs of similar molecular mass M and similar M distribution, PLCs have low viscosities and long relaxation times. Shear thinning viscosity occurs at low shear rates, somewhat similar to that caused by the occurrence of a yield stress, and apparently sometimes also at very high shear rates. Shear thickening appears occasionally. Little or no extrudate swelling occurs, despite high elasticity observed in small-amplitude oscillatory deformations. Thermotropic PLCs often can be processed with ordinary thermoplastic processing equipment. Because of low viscosities and low extrudate swells, this is even easier than processing of ordinary thermoplastics. Hence the name self-reinforcing plastics is sometimes used for thermotropic PLCs. This is not the case, however, for processing of lyotropic PLCs which usually requires special equipment and is fairly difficult.

Using the domain concept, Wissbrun[139] developed a theory of PLC flow. It is aimed mainly, but not necessarily exclusively, at longitudinal PLCs. The material is represented by a space-filling system of domains. At rest, the minimum energy arrangement is achieved when the directors in the planes of contacts are parallel (see *Figure 10a*). Under shear, domains slide over each other, as in *Figure 10b*. Wissbrun calculates the resulting stress and relates it to the fluid viscosity obtained from molecular dynamics (MD) simulations (the MD method is described for instance in Section 11.3 of reference 6). The model predicts shear sensitiveness: the curves of viscosity against shear rate are horizontal for low shear rates and then go down, and this with slopes comparable to experimental ones. The Wissbrun theory also leads to a shear-rate dependence of the normal stress, and to a correlation of viscosity with domain size. The model assumes that the domain size decreases by application of a stress, and is applicable until the domain size is larger than the length of a rod-like molecule or sequence. Then a plateau should appear in the viscosity *versus* shear rate curve, as was observed experimentally for HNA/0.73 PHB by Wissbrun, Kiss and Cogswell[140].

Interesting is rheology of a so-called twin PLC (TPLC), which is a longitudinal oligomer with a flexible centre and mesogenic sequences at both ends[141]. Two
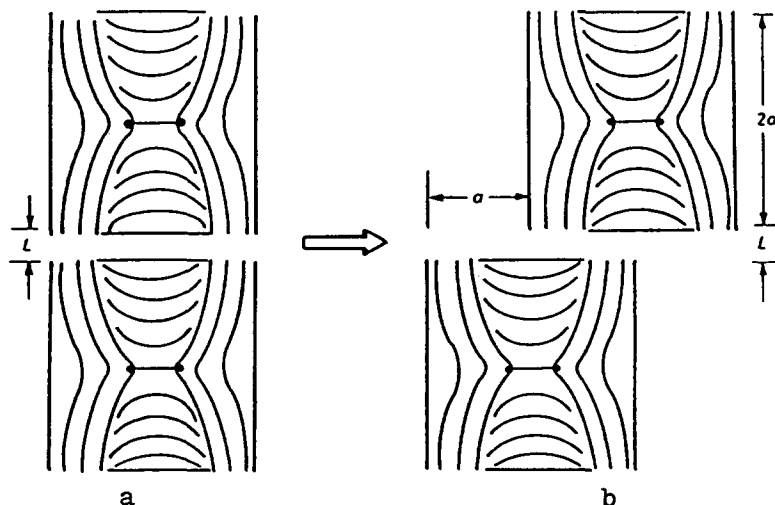

Figure 10 The Wissbrun model of domain flow of LC polymers (after Ref. 139). (a) two domains at rest; (b) the same domains in motion

phases are formed. Two mesogenic ends of a given TPLC molecule can be found within a single island, as in a *reentry molecule*, or they belong to two different islands as in a *tie molecule*. The latter act as physical cross-links, tying flexible sequences into a temporary three-dimensional network. For small amplitude deformations, the network shows high elasticity. As Winter and his colleagues explain[141], when strain amplitude increases, mesogenic ends are pulled out of the islands, the ratio of tie molecules to reentry molecules decreases, the network degenerates, and mechanical properties show a decay, that is a transition from elasticity-dominated to viscosity-dominated behaviour. This work represents another good example of how the properties can be affected by manipulating chemical structure.

PROCESSING OF PLCs AND MCs

Important advantages of melt processing such as in injection moulding of PLCs in comparison to ordinary engineering polymers were noted in previous sections. There is however, a difficulty shown in *Figure 4*. Using ordinary injection moulding equipment, one obtains a high degree of orientation of the skin, and little if any orientation in the core. Ophir and Ide[12] discuss four different layers in injection-moulded parts. Jansson, Gedde and collaborators[142] found either three or five layers in PET/0.6 PHB. Jackson and Kuhfuss[27] determined large differences in along-the-flow and across-the-flow mechanical properties of PEN/xPHB copolymers. Thin films exhibit particularly strong anisotropy, as reported in reference 27 and also found by Brostow *et al.*[115].

If one wants to manipulate anisotropy, several avenues are open. Ophir and Ide[12] advocate increasing the mould temperature to diminish anisotropy, with obvious consequences for costs. Multiaxial processing is possible. Chartraei, Macosco and Winter[143] developed an equibiaxial extensional flow technique involving lubricated squeezing between two parallel discs, used subsequently to advantage by Winter and collaborators[144–146]. A study of HNA/0.73 PHB shows[145] that preferred molecular orientation perpendicular to the compression (squeezing) direction is accompanied by random orientation within the plane of extension. Quenching immediately after high-temperature deformation retains this high degree of orientation. An alternative, which also gives a well-oriented material but with a higher degree of crystallinity, is stretching at 10–30 K below the melting point. One notes that such oriented samples show considerable strain recovery when reheated.

Blending and filling are of course possible. Duska[147] reports that 50% glass fillings and 50% mineral fillings of Xydar have lowered the skin/core effect, at the same time the processing windows became larger, while key mechanical properties are not much worse than those for neat PLC. Xydar is a copolyester based on p,p'-biphenol, PHB and terephthalic acid.

Another possibility is related to manipulating moulding geometry. Zachariades and Economy[148,149] have developed methods based on either injection moulding through a central port (*Figure 11a*) or cooling and simultaneously rotating one of the dies to introduce a curvilinear orientation (*Figure 11b–e*).

Two interesting processing techniques aimed at obtaining fibres with high anisotropy are discussed by Lewis
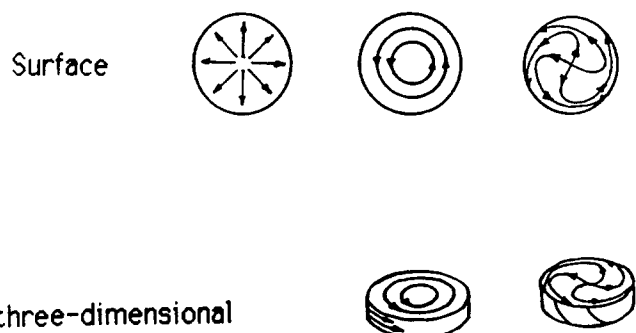
Figure 11 Polymer flow profiles (after Zachariades and Economy[148]): left, injection moulding; centre, rotational moulding; right, rotational injection moulding
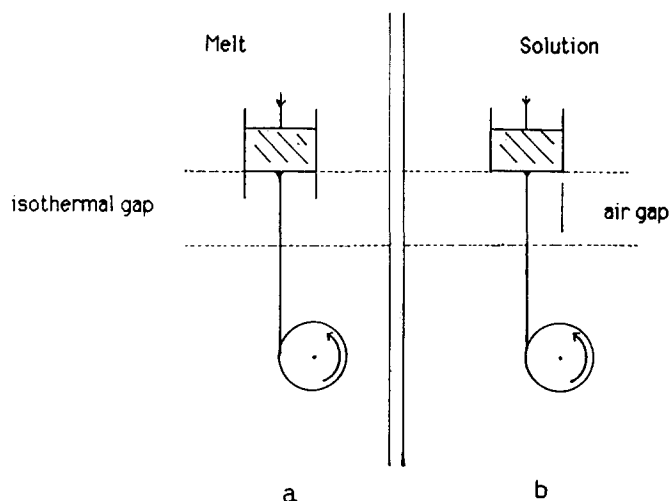
Figure 12 (a) Melt spinning and (b) dry-jet wet spinning (after Lewis and Fellers[150])

and Fellers[150]. One is called the melt spinning method, and the other, aimed at lyotropic PLCs and MCs, the dry-jet wet spinning technique. Both are shown graphically in *Figure 12*. The dry jet or air gap allows for elongational flow, which enhances the orientation of the LC material prior to its solidification in a coagulation bath. The melt-spinning analogy to the air gap is an isothermal gap at the die exit.

Earlier I characterized the Flory theory of thermodynamics and phase equilibria of binary and ternary systems containing rigid rod molecules. The guidance provided by the Flory theory is used, in particular, by Helminiak, Hwang and Wiff[151] in their development of improved methods of processing of molecular composites. Binary systems of rigid molecules dissolved in a solvent are here less interesting than ternary systems rigid polymer + flexible polymer + solvent. Processing and properties of both binary and ternary systems have been reviewed by Wiff, Helminiak and Hwang[151]. Because upon removal of solvent the resulting MC can be considered as blends, I shall return to them later.

CHARACTERIZATION OF PLCs

In this section I will discuss a few selected results and those methods of characterization which are particularly important for PLCs.

Given so many parameters that can be manipulated in designing PLC molecules, it is necessary to define the most important factors. Studies of Lenz[32] on polyesters show that flexible spacers are particularly important for thermotropic longitudinal molecules. The spacers reduce both the melting and the clearing temperatures. The type and length of the spacer can determine whether a nematic, cholesteric or a smectic phase is formed. In one particular series of polyesters, increasing the number of CH_2 groups in the spacer produces alternating nematic and smectic phases, and then above a certain length of the spacer only smectic phases are formed. Lateral substituents in the LC units also play a role. Two effects are also important here: steric hindrance by the substituents causes an increased separation of LC units on adjacent chains[32]; and interlocking by the substituent on adjacent chains occurs, causing a decreased mobility in the LC phase[152].

Conclusions reached by Lenz are pertinent not only for longitudinal PLCs. For instance, dramatic cases of interlocking were found by Diele *et al.*[153] for some inverse combs (Class κ, see *Table 1*). The resulting smectic A phases consist of layer structures with intercalating molecules.

The three types of order discussed earlier are important for understanding phase structures as well as phase transitions. On the basis of experiments including small-angle X-ray scattering and electric birefringence[154,155] Wendorff concluded that PLCs exhibit pre-transitional effects in the isotropic melts. In other words, orientational order characteristic for LC structures shows already in the isotropic liquid.

An interesting mesophase structure was found by Wendorff and collaborators[156,157] for a copolymer containing PHB, hydroquinone and carbonyl groups, and low concentrations of 4,4'-dihydroxybiphenyl and terephthalic acid units. On the basis of experimental results obtained by a variety of techniques, a rotationally disordered structure shown in *Figure 13a* was proposed. For comparison we show in *Figure 13b* the respective ordered structure.

Nuclear magnetic resonance (n.m.r.) and neutron scattering (n.s.) appear particularly fruitful for PLC characterization. In the study of dynamics of molecular reorientations the two methods complement each other[158]: deuterium n.m.r. provides information about long (more than 10^{-4} s) correlation times, while n.s. provides information about correlation times shorter than 10^{-8} s. Samulski[159] reviewed applications of deuterium n.m.r. to PLC studies, noting that one obtains information about structure of PLC molecules as well as about structures of the entire phases.

MLCs as well as PLCs exhibit the *odd–even* effect, visible for instance as a zigzag curve when plotting the
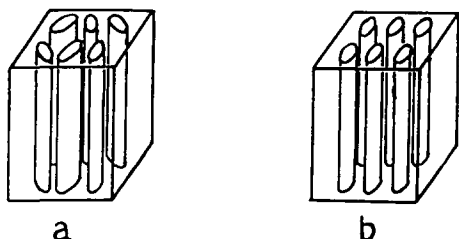
clearance or melting temperatures in function of the number of flexible bonds[82,160]. Blumstein, Blumstein and collaborators[160], using proton n.m.r. plus other techniques find that the effect is much stronger in longitudinal PLCs than in MLCs. In both cases, the explanation is in terms of the alignment of two consecutive LC units via a flexible spacer. The two LC unit axes fall alternately in and out of alignment as the length n of the spacer changes from even to odd. Also, both in MLCs and PLCs the librational reorientation and translational diffusion of mesogens are cooperative processes. Samulski and his colleagues[161] find with deuterium n.m.r. that the co-operativeness is stronger in longitudinal PLCs than in MLCs. In the former, a local order imposed locally on a segment is propagated intermolecularly to a remote chain site.

Comb PLCs with spacers were developed with the idea that the spacers will decouple different orientational tendencies of the backbone and the LC groups[48,49]. A deuteron n.m.r. study has confirmed[162] that the LC groups in the comb teeth are indeed relatively independent from the backbone. In two Subclass εO combs, in which the mesogens were labelled with ^2H at the terminal phenyl rings, the rings undergo 180° jumps about their local C_2-axes in the glassy state[163]. The reorientation of the entire mesogens is detected via the phenylene rings.

^2H n.m.r. can be also used to study binary systems in which flexible solutes adapt to the uniaxial environment of LCs. Janik, Samulski and Horiumi[164] studied per-deuterated *n*-alkanes in nematic solvents. They conclude that the rotational isomeric state (RIS) approximation, made so popular by work of Flory[165], is adequate, but a coupling between attractive and repulsive potentials would be worthwhile.

Finally, we shall note an important result obtained with n.s. Models had been developed for comb PLCs (Subclass εO) assuming a change in chain flexibility in nematic or smectic phases at phase transitions. Kirste and Ohm[166] showed by small-angle n.s. that the mean-square radii of gyration R_g do not change at phase transitions. However, one can define a directional R_g. In a macroscopically oriented nematic phase, R_g parallel to the orientation is smaller than R_g perpendicular to it.

DIELECTRIC PROPERTIES

I consider briefly dielectric properties separately because they reflect well molecular structures and also deformations, and thus are related to mechanical behaviour. Moreover, the ability of the electric field to orient PLCs, Class ε (combs) in particular, has far reaching applications: information storage[167]; optical elements such as Fresnel zone plates[168]; and non-linear processing[169,170]. In the linear approximation, electric charges are expected to be polarized proportionately to a perturbing electric field, regardless of how far these charges are from equilibrium, and regardless of any past optical perturbations of the system. As Meredith[171] exclaimed, 'This just can't be so, and isn't!' I have already referred to a review by Ulrich[107] of non-linear optical properties of rigid rod polymers.

The majority of mesogens have strong permanent dipole moments and thus are easily orientable by the electric field. The dielectric activity of polymers is usually discussed in terms of partial or complete dipole orientation polarization. The extent of orientational freedom of the

Figure 13 (a) Rotationally disordered and (b) rotationally ordered crystal (after ref. 156)

resultant dipole vector of polymer chains determines the degree of polarization. The dipole moments of various component groups, which together constitute the total resultant moment, may have different degrees of freedom. Thus, these groups achieve reorientation freedom at different temperatures, giving rise to various transition or relaxation processes.

Dielectric studies of PLCs have been initiated by Kresse and his colleagues[172-174] for combs. Subsequently, a number of further Class ε polymers were studied[175-184] along with a few of Class α[185-188]. Some lyotropic PLCs were studied by Moscicki and his colleagues[189-191]. In combs the dielectric relaxation spectra are determined mainly by the dynamics of the mesogenic units in combs' teeth. Then the dielectric anisotropy may be positive or negative, depending on the frequency of the directing electric field[179,180]. In longitudinal PLCs the dielectric spectra are typical for non-LC-polymers: fast processes corresponding to local segmental motions and much slower processes involving interchain cooperation.

Only one kind of lyotropic rod-like PLC was studied, namely poly-(n-alkyloisocyanate)s (PAIC) in toluene[189-191], but the results have potential industrial applications. The backbone chain of PAIC forms in solution a stiff, rigid helix. Therefore, the PAIC molecule has a very large permanent dipole moment $\approx 1000\,\text{D}$, and a very strong orientation in the field as a consequence. By comparison, a typical mesogenic unit has the dipole moment $\approx 2\,\text{D}$.

BLENDS AND THEIR PROPERTIES

For reasons stated earlier, PLCs and MCs have outstanding mechanical properties. An instructive illustration is shown in *Figure 14*. As compared to ordinary engineering polymers, they have also better thermal stability[106]. Ordinary polymers with high temperature resistance are typically processed with difficulty. By contrast, thermotropic PLCs are easily processed. For instance, poly(ester imides) with good thermal stability can be shaped into mouldings, fibres and sheets[192]. Thus, it is of interest to make PLC-containing blends which would have these good properties and are available in
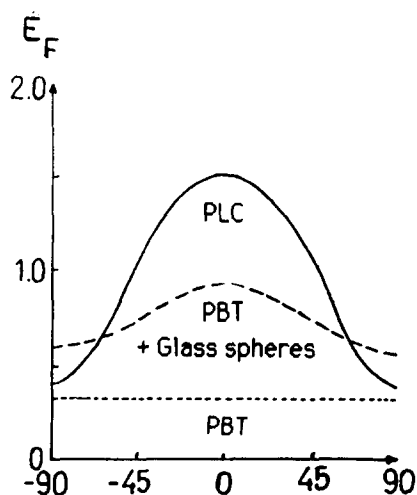

Figure 14 Distribution of flexular modulus E_F (in arbitrary units) as function of the test direction angle for poly(butyl terephthalate) (PBT), PBT filled with glass spheres and a PLC (after ref. 12)

large quantities at reasonable prices. In addition to applications based on mechanical, thermophysical, rheological or electrical characteristics, LCs have also applications based on their structures, as in LC-blend membranes for separation processes[193]. When making blends, the existing understanding of MLCs, on which excellent books exist[194,195], might be of help.

I shall now consider LC blends and their properties in terms of methods of processing them, solution *versus* melt, starting with the former. There are two basic ways of obtaining rigid-rod containing polymer blends. In the first, a rigid material, LC or otherwise, is mixed with a flexible polymer and with a solvent. That procedure leads to MCs, as developed and reviewed by Helminiak, Wiff and their collaborators[151]. The second consists in using a PLC + ordinary engineering polymer + solvent.

The idea of mixing rigid rod polymers with ordinary ones is, of course, based on heterogeneous composites (HC). Having found a suitable solvent, the rigid molecules have to be individually dispersed in a flexible polymer matrix; this can be achieved, and automatically provides a much better degree of cohesion than in any HC. Phase separation under shear has to be avoided. Under proper conditions, entanglements in the flexible component provide integrity to the blend made by solution casting. The blend has properties similar to an elastomer[151].

The second way, that of mixing a PLC with an engineering polymer in a solvent, is being used in particular by Kosfeld, Hess and collaborators[196-198]. They have studied ternary phase diagrams PET/xPHB + poly(bisphenol-A-carbonate) + CHCl$_3$. As in the case of work of Helminiak and Wiff, theoretical guidance is provided also by the Flory theory[130-134]. However, the theory is less applicable here because the PLC molecules are only partly rigid, and differences between predicted binodals and measured cloud point curves are found[196]. Isothermal cloud point curves seem to lie between spinodals and binodals. The blend is a multi-phase system. There is a certain amount of the PET/xPHB copolymer in the polycarbonate (PC)-rich phase, while PC is almost completely excluded from the copolymer-rich phase. Annealing in the melt causes transesterification, and this improves compatibility[198]. Thus, in making blends we have to consider not only properties' of the components, but also potential chemical reactions between them.

Several groups have undertaken studies of AB + C blends, where A is the flexible component of a copolymer, B the LC component, and C an engineering polymer. Thus, Siegmann *et al.*[199] worked with a LC co-polyester made by Celanese Corp. (now Hoechst-Celanese) blended with an amorphous polyamide. Somewhat similar to the results shown in *Figure 9*, the melt viscosity became lower upon PLC addition, and the viscosity decreased when the shear rate increased. In a two-phase system, adhesion between the phases was good while tensile behaviour was similar to heterogeneous composites. Kiss[200] mixed a polymer with a high glass transition temperature, namely polyethersulphone (PES) with a number of polyesters and poly(ester amides) made by Celanese. A considerable reinforcement of PES was found in terms of tensile strength, flex strength and flex modulus, while again processing was easier. Weiss and collaborators[201] mixed polystyrene (PS) with a nitrogen-containing longitudinal PLC. The components are immiscible, but elongational flow produces a fibrous PLC
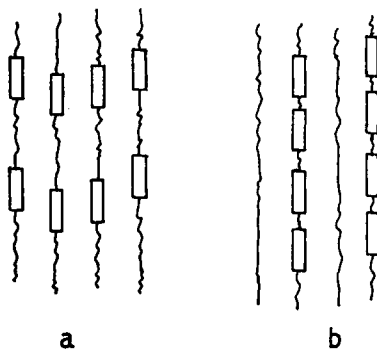
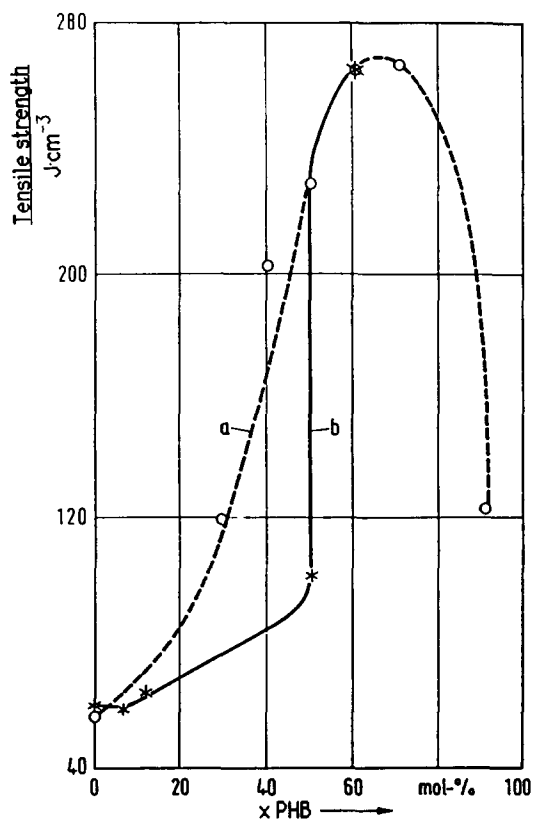**Figure 15** Fragment of (a) a pure liquid–crystalline copolymer; (b) a blend containing the same copolymer

Figure 16 Tensile strength for the PTE/xPHB system in function of LC mole concentration x (after ref. 9). $J\,cm^{-3} = N\,mm^{-2} = MN\,m^{-2} =$ MPa. - - -, pure copolymers; —— blends

phase which persists after solidification. A small amount (4.5%) of PLC in the material produces a 40% increase of the tensile modulus as compared to pure PS. Weiss is preparing a review[202] on blends containing PLCs.

Brostow *et al.* have studied among other things a simple AB + A type system[9,15]. They took the PEN/xPHB of Jackson and Kuhfuss, and mixed it with PET. Both the pure copolymer and the blends are two-phase systems. To see advantages of the simplicity, consider a pure PLC copolymer, as shown schematically (with some chain alignment) in *Figure 15a*, and compare it with a blend, *Figure 15b*. The blend does not contain any new kinds of chain segments. They achieve the same overall concentration of the LC component in a pure copolymer and in a blend, but the modes of energy transmission under mechanical load should be different. While their studies involve a variety of techniques and properties

(injection and compression moulding, solution casting, calorimetry, thermogravimetric analysis, rheology, mechanical testing, electron scanning microscopy of the fracture surfaces), I shall consider here only one significant result. In *Figure 16* I show the tensile strength for copolymers (broken line) as well as blends (solid line). This shows that in a considerable concentration range the strength of the blends is lower than that of the copolymers. Looking at *Figure 15b* again, it can be seen that the lines of force must be avoiding the islands shown in *Figure 5*, as the islands offer more resistance because of their rigidity. Only when the concentration of the LC component is such that the islands are too numerous and/or too large to be avoided (the phase inversion is approaching), the tensile strength of the blends shoots up and joins the curve for pure copolymers. However, even when the tensile strength of the blend is lower than that of the copolymer with the same LC contents, it is still distinctly higher than that of the pure engineering polymer, PET in this case.

CONCLUDING REMARKS

I have noted very useful thermophysical, dielectric, optical, rheological and mechanical properties of PLCs and MCs, as well as their good dimensional stability, low flammability and good chemical resistance. This list is by no means complete. Jones and collaborators have developed good PLC coatings for non-bake applications, some of them εO combs[203–205] and some crosslinked[82,83]. In an entirely different area, certain smectic phases show ferro-electric as well as pyroelectric properties[206,207]. These have been proposed for use in optical shutters because of their fast switching speeds and bistability, as well as in displays and heat sensors.

One finds that properties of ordinary engineering polymers can be largely improved by blending with thermotropic polymer liquid crystals, usually with melt processability improved at the same time. The fact that LC-containing materials are typically biphasic is not a disadvantage. The predominantly flexible phase contains some LC sequences, and they provide a certain amount of reinforcement; much more reinforcement is caused by the LC-rich islands. Costs are lower as compared to the use of pure liquid crystalline materials. Blends should find applications in electrical, electronic, chemical, aircraft, aerospace and automotive industries, and this list of interested industries is not complete either.

I have shown the variety of molecular structures that can be realized. In view of this variety, most developments in the field of PLCs, MCs and their blends, basic research as well as industrial applications, are still before us.

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