Thermotropic hexagonal phases in polymers: common features and classification[*]

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Polymeric mesophases with positional order in two dimensions are considered in relation to the established liquid crystal phases. It is proposed that the mesophase with hexagonal symmetry observed in polymers as flexible as polyethylene and poly(diethylsiloxane) is columnar liquid crystal. The relationship is discussed with columnar phases in non-discotic low molar compounds and, particularly, with polymers like poly(dialkylsilane)s or alkylated polyglutamates. It is argued that the presently considered hexagonal phases are properly classified as liquid crystalline in spite of the absence of both rigid moieties and amphiphilic character from some of the polymers concerned. Since the phases described here have in the past prompted the introduction of 'condis crystals' as the third class of mesophases, alongside plastic and liquid crystals, some comments are made about the general classification of mesomorphic states.

(Keywords: columnar liquid crystal; discotic liquid crystal; hexagonal phase; mesophase; condis crystal; plastic crystal; sanidic phase; two-dimensional order; phase classification)

INTRODUCTION

Reports have been mounting over the years of a number of unconventional phases, which apparently do not fit the established classification of states of matter intermediate between the ordered crystal and isotropic liquid. Amongst these are phases with hexagonal symmetry[1], 'board-like' phases[2,3], etc. The questions of the exact nature of translational order, of the relationship with other established states of matter and of classification of these phases, remain controversial.

The 'hexagonal phase'[†] has been observed in a number of disparate polymers, such as polyethylene[4–9], 1,4-t-polybutadiene[10,11], fluoropolymers and copolymers[12–16], alkylated polysiloxanes[17–19], polyphosphazenes[20–25], polysilanes[26], etc. It has not received a unified treatment, except for the work of Wunderlich and collaborators[1,27] who described it as 'condis crystal' (see below). Otherwise, at different times and in cases of different specific polymers, it has been termed 'rotator'[28], 'liquid crystal'[29], 'smectic'[14,30], 'high temperature' or 'hexagonal' crystal form[10], 'visco-crystalline'[17], 'thermotropic'[23], 'columnar'[31,32] or simply 'mesophase'[19]. The features which have puzzled many researchers are the absence from most macromolecules that exhibit the hexagonal phase of rigid rod-like or disc-like mesogens and often also of amphiphilic character; the presence of at least one of these features is normally assumed essential for the formation of thermotropic liquid crystals.

In view of the importance, scientific but also technological, of the widespread hexagonal phase in polymers, it is necessary to re-examine the experimental information on this phase in the light of the exacting classification criteria of condensed matter.

THE HEXAGONAL PHASE IN POLYMERS

Occurrence

The first examples of the disordered 'hexagonal crystal form' were reported in the early 1960s for poly(tetrafluoroethylene) (PTFE) (form I above 30°C)[12] and for 1,4-t-polybutadiene (form II, thermodynamically stable above 83°C)[10,11,33]. Since then, a similar form has been found in numerous diverse polymeric systems (*Table 1*). Comprehensive pre-1988 information on phases with conformational disorder, which include most of the presently discussed hexagonal polymeric phases, has been compiled by Wunderlich and collaborators[1]. The reader is also referred to the review of polysiloxanes and polyphosphazenes by Godovsky and Papkov[19].

We note that there are three types of macromolecules which form the hexagonal mesophase (*Table 1*):

1. flexible linear macromolecules: PTFE and related halogenated polyethylenes, 1,4-t-polybutadiene, 1,4-*cis*-poly(2-methylbutadiene), polyethylene (linear polymer and some copolymers), poly(*p*-xylylene), biphenylethane (BPE)-containing main chain copolymers;
2. flexible branched (comb-like) macromolecules: alkyl-branched polysiloxanes, polysilanes and polygermanes, aryl- and some alkyl-branched polyphosphazenes, poly(vinyl trimethylsilane);
3. rigid macromolecules with flexible side chains: n-alkyl substituted poly(L-glutamate) and cellulose.

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[†] The term 'hexagonal phase' as used here should not be confused with the hexagonal phase formed by cylindrical micelles in lyotropic systems

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Table 1 Non-discotic polymers exhibiting a thermotropic two-dimensional hexagonal phase

Polymer	Common name	Temperature interval (°C)	Ref.
Group A			
Polyethylene (PE)			
at high pressure (triple point 3.5 kbar, 215°C)	Anabaric, hexagonal	280–307 (at 8 kbar)	4–6, 83
constrained ultra-oriented fibres	Hexagonal	155–180	7, 8
irradiated	Hexagonal	60:130–100:135[a]	9
PE with short branches			
ethylene–propylene copolymer	Hexagonal	<60	9
ethylene–vinyl chloride copolymer	Hexagonal	<20:54	106
1,4-t-polybutadiene $(-CH_2-CH{=}CH-CH_2-)_x$	Form II	83–164	10, 11, 33
1,4-*cis*-poly(2-methylbutadiene) $(-CH_2-\underset{CH_d^3}{C}{=}CH-CH_2-)_x$ (*cis*-polyisoprene) above 2.5 kbar (metastable)	High pressure phase	>20	35, 36
PTFE $(-CF_2-CF_2-)_x$	Form I	30–330[b]	12, 13
Tetrafluoroethylene–hexafluoropropylene copolymer		> −40	16
P3FE $(-CF_2-CHF-)_x$		<r.t.–193:209	14, 84, 85, 107
VDF–trifluoroethylene copolymer (50–80% VDF)	Paraelectric phase	70:150–150:160	15
Poly(*p*-xylylene) $(-Ph-CH_2CH_2-)_x$	β_2	280–420	28
Polyethers of BPE (BPE-*m,n*) $(-Ph-CH_2CH_2-Ph-O-(CH_2)_{m,n}-O-)_x$ and	Columnar	104–181	108
fluorobiphenylethane (FBPE-*m,n*) $(-\underset{F}{Ph}-CH_2CH_2-Ph-O-(CH_2)_{m,n}-O-)_x$		110–140	110
BPE–FBPE copolymers		100–180	110
Group B			
Poly(dialkylsiloxane)s $(-\overset{R}{\underset{R}{Si}}-O-)_x$ $R = C_2H_5, C_3H_7 \ldots$	α_m, μ	−50:+40–50:200	17–19
Polyphosphazenes $(-\overset{OR}{\underset{OR}{P}}{=}N-)_x$ $R = F_3C-CH_2$ or aromatic	δ	150:180–360:400	20–25
Poly(dialkylsilane)s $(-\overset{R}{\underset{R}{Si}}-\overset{R}{\underset{R}{Si}}-)_x$ $R = n-C_4H_9$ through $n-C_{14}H_{29}$	Phase II, columnar	10:80–>450	26, 31, 111
Poly(dialkylgermane)s $(-\overset{R}{\underset{R}{Ge}}-\overset{R}{\underset{R}{Ge}}-)_x$ $R = n-C_8H_{13}$		>15	112
Poly(vinyltrimethylsilane)[c] $(-CH_2-\underset{Si(CH_3)_3}{CH}-)_x$			59
Copolysiloxanes with forked side groups	Columnar	<97	91
Polysiloxanes with hemi-phasmid side groups		<193	88
Poly(vinyl ether)s with hemi-phasmid side groups		<90	89, 90
Group C			
Poly(n-alkyl-L-glutamate)s $(-NH-\underset{CH_2CH_2COO(CH_2)_nH}{CH}-CO-)_x$ $n = 4–18$	$n<8$:'2-d hex.' $n>10$:'Region B' $n=18$:'Columnar'	40:130–200 −24:+62–30:64	92, 94
Cellulose tri-n-alkanoates $n = 8–18$	Columnar	60:90–100:120	93

[a] $T_{crystal-columnar}$ (lower:upper bound) – $T_{columnar-isotropic}$ (lower:upper bound) of most polymers in the range

[b] See text

[c] Some uncertainty about true absence of longitudinal positional LRO

In most listed polymers the hexagonal phase appears at atmospheric pressure and without any special treatment. In polyethylene either high pressure is required[4–6] or crosslinking[9], or introduction of short chain branches[9,34], or else the oriented polymer must be heated while mechanically constrained[7,8].

It should be stressed that in all cases listed in *Table 1* the hexagonal phase is the stable equilibrium state in a given temperature (and pressure) range, and is enantiotropic. The two exceptions are 1,4-*cis*-poly(2-methylbutadiene), whose hexagonal phase occurs only because the nucleation of the ordered crystal is greatly inhibited at elevated pressures[35,36] and the high-temperature phase in constrained ultra-drawn polyethylene fibres, where the hexagonal phase persists for as long as it takes the extended high molecular weight chains to diffuse and acquire the stable random coil conformation of the isotropic melt. Nevertheless, even this transient polyethylene phase survives long enough for the reverse transition to the orthorhombic crystal to be observed with the use of synchrotron X-ray radiation[37]. The lifetime of the hexagonal phase can be substantially extended if the polymer is initially lightly crosslinked, thereby inhibiting fibre retraction by molecular diffusion; in that case the hexagonal–orthorhombic transition can be observed even with the use of a conventional X-ray source[38].

Properties of the hexagonal polymeric phase

A detailed discussion of several aspects of the presently considered systems, especially their thermodynamics, can be found in the review by Wunderlich *et al.*[1]; thus thermodynamical features will not be elaborated here. As far as classification is concerned, the main distinguishing feature of the currently discussed hexagonal phase is the absence of positional long range order (LRO) in the chain direction and, accordingly, the lack of crystallographic register along this direction. Thus the phase is positionally two-dimensionally ordered. As discussed later, X-ray fibre diffraction patterns only show sharp Bragg-type $hk0$ reflections, while only diffuse streaks are observed on layer lines with $l \neq 0$. As expected, it would appear that these hexagonal phases do not support static shear stress. The measured dynamic shear modulus is indeed very close to that of the melt[39]. There are, of course, a number of examples of three-dimensional crystalline phases with hexagonal symmetry in different polymers, but these are not the subject of the present paper.

One common property of the hexagonal polymeric mesophase is some degree of conformational disorder, either in the main chain or in the side groups or in both. This has been well documented, chiefly by n.m.r.[40–42] and by vibrational spectroscopic methods[43,44]. Compared with the ordered crystalline state, there is a high degree of molecular mobility, with the chain performing both rotational and translational motion[45]. Translational chain mobility enables easy formation of extended chain crystals in polymers that exhibit the mesophase; isothermal extension of the initially folded chains has been shown to occur in the mesophase[46–52]. Time-resolved synchrotron SAXS experiments have shown rapid thickening of solution-grown chain-folded crystals of poly[bis(*p*-methylphenoxy)phosphazene][53] and 1,4-t-polybutadiene[54] immediately upon the phase transition into the mesophase.

The hexagonal polymeric phase is potentially of considerable technological importance. It has interesting rheological properties as it enables 'melt' processing of high molecular weight polymers, as demonstrated on PTFE[30], polyethylene[55] and polyphosphazene[56]. While the true isotropic melt of such polymers is intractable, due to the high degree of chain entanglement, the self-disentangled chain-extended mesophase facilitates the shear. The effectiveness of the hexagonal phase in these flexible polymers in reducing the viscosity of isotropic melt can, in fact, be greater than the equivalent and well publicized effect of nematic ordering[57].

The hexagonal phase transition in some polyorganosilanes and germanes is associated with a change of colour (thermochromic transition), and there are interesting optical and electrical properties displayed by these polymers due to their σ-conjugated backbone[58]. A further example of a useful property of the mesophase is the high gas permeability of poly(vinyl trimethylsilane) in the glassy hexagonal state; this can be exploited for the production of oxygen-enriched membranes[59].

Ambiguities in classification

As mentioned in the Introduction, attempts to classify the hexagonal polymeric phase have led to considerable disagreements. For example, to describe it as a 'rotator crystal', 'visco-crystal' or, indeed, any type of crystal, ignores the two-dimensional nature of the hexagonal phase, i.e. its lack of positional LRO in the chain direction. The same objection also applies to it being labelled as a 'condis crystal', as this term implies 'dynamic conformational disorder and long range positional and orientational order'[1].

While it is tempting to relate the hexagonal phase to the hexagonal packing of molecules in smectic B phase, the other essential feature of a smectic phase, the periodic density fluctuation forming 'layers', is not found in hexagonal polymers. The usual stacking of lamellar crystals, or mesophase domains, in polymers cannot be equated with smectic layering since the former are non-equilibrium structures resulting from the growth kinetics. It is appropriate at this stage to review briefly the presently accepted classification scheme and classification criteria for semi-ordered condensed matter. This should help in deciding whether or not the main features of the present polymeric hexagonal phase fit an already existing phase type.

ASSESSMENT OF EXISTING MESOMORPHIC STATES

Criteria for classification

Translational symmetry, i.e. the existence and dimensionality of positional and orientational LRO, is the primary criterion which distinguishes different states of condensed matter. While at one end of the spectrum the crystal has both positional and orientational LRO in all three dimensions, isotropic liquid, at the other end, has none; all intermediate cases are designated as liquid crystal[60–62].

Liquid crystals

Since the polymeric hexagonal phase of present concern lacks positional LRO in one dimension, it can be safely classified as liquid crystalline. The question as

Table 2 Phase classification in terms of translational symmetry

	Dimensionality of long-range order			
	Mol. orient. order[a]	Bond orient. order[a]	Positional order	Phase
Isotropic liquid	0	0	0	Isotropic
Liquid crystal				
Nematic	1	0	0	Uniaxial
	3	0	0	Biaxial
	1	0	1[b]	Sm A
Smectic (Sm)	3	2	1[b]	Sm C
	3	2	1[b]	Hexatic phases (hexatic B, Sm F, Sm I)
Columnar	3	2	2	Columnar
Crystal				
				Ordered smectics (crystal B, G, J, E, H, K)
				Sm D (cubic)
Disordered	3	3	3	Plastic
				Other orientationally and conformationally disordered
Ordered	3	3	3	Ordered

[a] Note the distinction between molecular and bond orientational LRO. The former refers to the orientation of a tensorial quantity associated with the molecule itself, like moment of inertia or polarizability. The latter refers to the orientation of the vector joining two neighbouring molecules

[b] QLRO (correlation decays algebraically, and asymptotically approaches zero with increasing distance; in LRO it descends to a finite value)

to which existing category of liquid crystals this phase should belong is best addressed with reference to *Table 2* which attempts to summarize the current state of mesophase classification[60–62].

According to the dimensionality of positional order, thermotropic liquid crystals can be divided into three large classes: nematic, with no positional LRO; smectic, with quasi long range order (QLRO)[63] in one direction; and columnar, with apparently true LRO in two dimensions[64]. The latter is the obvious candidate for the hexagonal phase in polymers, particularly since the majority of known columnar liquid crystals have hexagonal symmetry[65].

While nematics and smectics are further subdivided according to dimensionality of molecular orientational and bond orientational order (for explanation see *Table 2*), all columnar phases apparently share a common basic level of symmetry. Variations amount only to differences in planar symmetry (see below).

It is now becoming increasingly accepted that the hexagonal phase in branched polymers of groups B and C (*Table 1*) is columnar liquid crystal. This acceptance is aided by the fact that chemical character of the backbone differs from that of the side groups, which has its analogue in the amphiphilic character of most low molar columnar systems. However, the columnar liquid crystal nature of unbranched molecules of group A (*Table 1*), such as polyethylene, is not yet generally appreciated.

Condis crystals

Here a comment is due on a somewhat different classification principle[1,27], which divides the area between the ordered crystal and the isotropic liquid into three parallel classes, namely liquid crystals, plastic crystals and condis crystals. Since it has been proposed that most of the phases with two-dimensional order described in this paper are condis (*con*formationally *dis*ordered) crystals[1], some comments should be made on this alternative classification.

First, it should be pointed out that the definition of condis crystals is not primarily based on symmetry, but rather on the existence of a degree of conformational disorder. We note that some equilibrium disorder (vacancies, wrong orientations, etc.) is always present in crystals at finite temperatures and, for complex flexible molecules, the same applies to conformational defects. However, this in itself should not warrant placing such crystals in a separate category.

We propose that the term 'condis crystal' be reserved only for those crystals in which, due to conformational disorder, some or all of the atoms lack a single preferred position in the unit cell. In a condis crystal thus defined, the symmetry of a time-averaged molecule is higher than the symmetry of any individual molecular conformation. A good example, chosen by Wunderlich *et al.*[1], and which also fits the presently proposed definition of condis crystals, is *p*-terphenyl[66], where the averaged molecular conformation, as 'seen' by X-ray diffraction, has a mirror plane passing through the terminal benzene rings, although the middle ring spends most of the time in one of the two equivalent potential minima corresponding to a tilt of ±30° away from that plane. This and numerous other examples, including crystalline phases of liquid crystal forming molecules containing disordered alkyl moieties, or high temperature phases of aromatic polyesters, should be considered as legitimate examples of condis crystals.

Defined as presently proposed, condis crystals have a distinct identity, but should be regarded as belonging to the wider class of disordered crystals, together with orientationally disordered crystals, from which they often cannot be separated. Outside the category of three-dimensional crystals, the condis phase concept is ambiguous, since almost all liquid crystals implicitly possess some degree of conformational disorder.

As a final comment on the division of mesophases into plastic, condis and liquid crystals, we note that plastic crystals[67,68] are only a special case of orientationally disordered crystals[69] originally defined, rather arbitrarily, as having cubic symmetry and an entropy of fusion less than 5/2 R[70]. Thus it would appear that neither condis nor plastic crystals can occupy an equivalent place alongside liquid crystals in the classification scheme of condensed matter.

Discotic and non-discotic columnar phases in other systems

Columnar phases were first described in 1977 in low molar systems of disc-like molecules[71], hence the

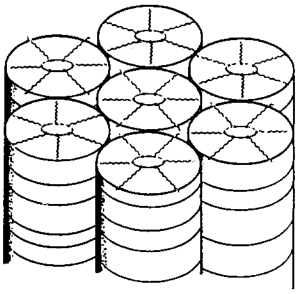


Figure 1 Schematic drawing of molecular stacking in a discotic hexagonal columnar phase. From reference 113. Courtesy of the Royal Society of Chemistry

alternative term 'discotic phase'. In the columnar mesophase the discs are stacked on top of each other to form columns, which in turn are packed on a two-dimensional, usually hexagonal, lattice (*Figure 1*). Discotic columnar phases have been reported in a few polymers which contain disc-like mesogens either in the main chain[72] or as side groups[73,74]. These are not discussed here as we are dealing with the non-discotic polymeric columnar phase.

More recent work has shown that, even within the field of low molar liquid crystals (LLC), columnar phases can be formed by non-discotic molecules. Columnar liquid crystals are also formed by the so-called 'phasmids' and 'biforked' molecules[75–77]. Thermotropic columnar phases are also found in a number of 'neat' soaps[78], where the important driving force is the microphase separation between the hydrophilic and hydrophobic molecular moieties. Following a similar principle, columnar, or cylindrical, phases also occur in lyotropic systems of amphiphilic molecules, such as soap–water systems[79].

Most pertinent to the present discussion is the case of highly concentrated solutions of two rigid helical polymers: DNA and the synthetic polypeptide poly(γ-benzylglutamate) (PBG). Concentrated water solutions of DNA form a hexagonal columnar phase in which molecular helices propagate along the column axis[80,81]. Recently it was inferred from optical textures that a similar arrangement may also exist in racemic PBG solutions[82].

POLYMERIC COLUMNAR PHASE

Diffraction pattern and the type of disorder

As already mentioned, X-ray scattering patterns of oriented columnar polymers show sharp diffraction maxima on the zeroth layer line. On non-zero layer lines only diffuse scattering is observed, see *Figures 2* and *3*[12,83]. These features are consistent with the existence of true LRO in the two-dimensional hexagonal arrangement of molecular axes, and with the absence of long range intermolecular correlation along the chain direction. It should be noted that the latter also implies the absence of true LRO along the chain, or column[84]. In spite of this absence of true intrachain LRO, comparatively sharp meridional scattering maxima can occasionally be seen, particularly in less flexible polymers.

The streaks of continuous scattering on non-zero layer lines confirm that the molecules remain parallel and indicate the existence of short helical sequences.

The equatorial hexagonal reflections can be rather numerous (up to 10 or more in 'form I' of PTFE and copolymers, see *Figure 3*), but more often, only one intense (1 0 0) and two weak (1 1 0 and 2 0 0) reflections are observed. If the disorder were purely translational along the chain axes, high order equatorial reflections, such as those seen in the crystal phase, would be preserved[12], since it is only the projection of the molecules onto the plane normal to their axes that affects equatorial intensities. However, in the columnar phase of most polymers both rotational and conformational disorders seriously weaken higher order reflections.

Excursions from chain linearity, i.e. the presence of positional disorder, also reduces high order reflections, and this effect is generally more important in more flexible polymers [e.g. polytrifluoroethylene (P3FE)[85] or polyethylene, cf. *Figure 2*), as opposed to PTFE.

Some abiguity remains as to whether phase I of PTFE is truly columnar at 30°C or whether it still has some three-dimensional positional order. While the X-ray photograph of phase I presented by Clark and Muus[12] (*Figure 3*) shows only diffuse scatter on all but the zeroth layer line, the authors claim that oscillation photographs show additional sharp reflections on the 15th layer line, referring to the 15/7 helix of the crystalline phase IV.

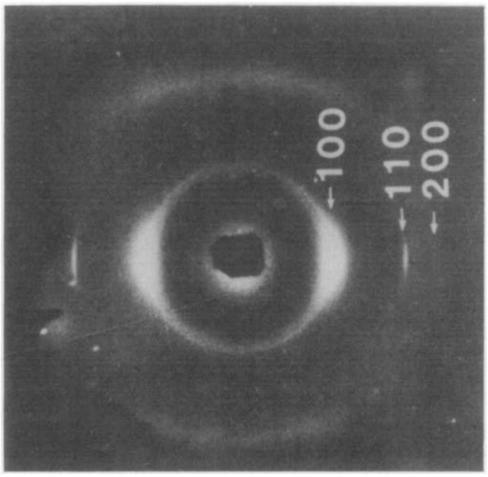


Figure 2 Fibre diffraction pattern of the high-pressure hexagonal phase of polyethylene. Fibre axis is vertical. From reference 83. Courtesy of Marcel Dekker, Inc.

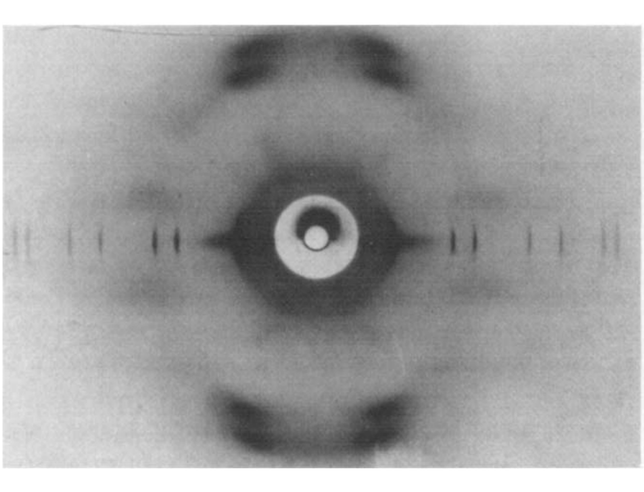


Figure 3 Fibre pattern of phase I of PTFE (30°C). The fibre axis is vertical. From reference 12. Courtesy of Oldenbourg Verlag

Note that the reflections on both the zeroth and 15th layer lines are dominated by the zeroth-order Bessel function, and are thus least susceptible to rotational disorder. If the *h*,*k*,15 reflections signify genuine three-dimensional LRO, this would in fact mean that the *c*-dimension of the crystal unit cell is reduced by a factor of 15, i.e. to only 1.3 Å upon the 30°C transition from phase IV to phase I. Such a crystal, with a unit cell containing only one CF_2 group, would fall in the category of condis crystals according to the definition given earlier, since its high symmetry (small unit cell) would be a consequence of conformational disorder. In a subsequent paper[16], Clark *et al.* suggest that longitudinal order in phase I of PTFE is lost above 100°C, which may imply that columnar order only exists above that temperature.

At the same time, in a study of a random copolymer of tetrafluoroethylene and hexafluoropropylene (TFE–HFP) it was found that the random placement of CF_3 groups helps destroy the longitudinal order. No sharp *h*,*k*,15 reflections were observed in the copolymer at any temperature, hence the copolymer is truly columnar. Similarly, true columnar phases exist in P3FE[14,84,85,107] and in trifluoroethylene–vinylidenefluoride (VDF) copolymer above the ferroelectric Curie temperature[15].

Molecular structure and flexibility

Comb-like macromolecules with flexible backbone. Of the polymers listed in *Table 1*, the ones with flexible side branches (groups B and C) are most easily visualized as forming columns similar to those in LLCs. Indeed the first reference to a thermotropic hexagonal phase in a non-discotic polymer as 'columnar' was made in conjunction with poly(di-n-hexylsilane)[31], a member of group B. Both in comb-like polymers and in discotic LLCs the side groups form the peripheral section of the columns. Two important differences remain: in polymers there is molecular connectivity along the column axis, absent in LLCs; and there may be a total absence of any rigid units (disc- or rod-like) in polymers that form columnar phases.

While there is no detailed theoretical treatment of the columnar phase in polymers, in the case of comb-like macromolecules with long alkyl side groups the two-dimensional ordering is rather easily understood in simple qualitative terms. As aliphatic chains melt at or above room temperature a disordered sheath is formed around the backbone which screens off the periodic nature of the polymer chain from its neighbours. Thus intermolecular positional register is lost along the chain direction. At the same time, since an isolated one-dimensional lattice cannot possess LRO[84], a flexible polymeric backbone would be conformationally disordered in a columnar phase. In this way the conformations of the main chain and side chains are directly linked. In principle, the 'molten sheath' concept is also applicable to rigid backbone polymers with long side chains (group C in *Table 1*).

The poly(di-n-alkylsiloxane) family can be considered as bridging the gap between groups A and B, since even the member with ethyl side groups exhibits the columnar phase. The 'molten sheath' interpretation given above is not credible for such short side groups, although microphase separation between the organic side groups and inorganic backbone has been invoked. It is likely that, as in linear polymers of group A, flexibility of the backbone itself plays an important part in destroying positional order in the chain direction and leaving only the two-dimensional columnar lattice. Molecular mechanics calculations for isolated polydiethylsiloxane chains[86], as well as n.m.r. work[42,87], indicate the link between the ethyl substituent and the conformation of the flexible siloxane backbone.

Hexagonal columnar phase has recently been found in polymers with side groups containing hemi-phasmid mesogenic units which consist of a rod and a half-disc[88,89] or only a half-disc at the outer end[90]. As with phasmids (see earlier) the half-disc contains three flexible tails emanating from an aromatic ring. The polymers which so far showed the columnar phase had polysiloxane, poly(vinyl ether) and polymethacrylate backbones. The proposed column structure consists of a bundle of backbones threaded through the centre of the column, from which the side groups radiate outwards; thus an intermediate aromatic cylinder and an outer aliphatic sheath are formed (*Figure 4*).

The effect of the degree of polymerization (*DP*) on isotropization temperature can be complex in hemi-phasmid polymers. Thus T_i sometimes has a maximum at $DP = 4–5$, suggesting that a self-assembled disc containing four to five monomer units with ring-like backbone is the most stable conformation[89]. Other unusual phenomena, such as a re-entrant isotropic phase, were also observed in these systems.

The columnar phase has recently also been found in a copolymer containing forked mesogens as side groups[91]. Forked mesogens contain two flexible chains rather than three as in hemi-phasmids. Interestingly, the hexagonal phase was not observed in the homopolymer[91].

It may be mentioned that the analogous small molecules of the 'biforked' type sometimes form smectic and sometimes columnar phases[77]. This would indicate that it is the overcrowding of the aliphatic layer in a potentially smectic arrangement which forces a phasmidic system to form cylinders, having a larger surface-to-volume ratio. Indeed, polysiloxanes with hemi-phasmid side groups were found to form columns only if the alkyl chains were sufficiently long (e.g. dodecyl)[88]. Shorter chains (e.g. pentyl) gave a smectic phase.

Comb-like macromolecules with rigid backbone. Thus far, two groups of macromolecules of this type, exhibiting a thermotropic columnar phase, have been described. They are synthetic polypeptides poly(n-alkyl glutamate)s[92] and n-alkyl triesters of cellulose[93].

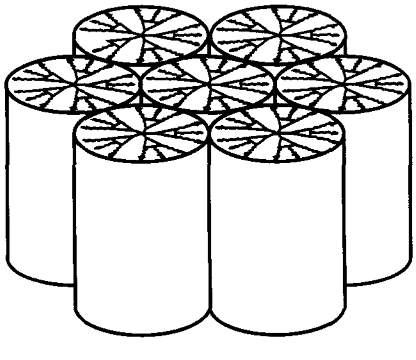


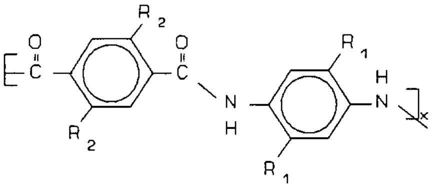
Figure 4 Molecular organization in the columnar phase of polymers with tapered hemi-phasmid side groups (schematic). The bundle of backbones is threaded through the column axis. The triangles denote the aromatic moieties each anchoring three flexible outer chains

In poly(n-alkyl glutamate)s intramolecular hydrogen bonding gives rigidity to the helical backbone, onto which flexible n-alkyl side groups are appended. According to their phase behaviour, these polymers can be divided in two groups: those with short side chains ($n<8$) and those with long side chains ($10<n<18$)[92]. For polymers in the first group, the low temperature three-dimensional hexagonal modification loses longitudinal register and becomes two-dimensional above the temperature of the α-relaxation transition. For polymers with $10<n<18$ the two-dimensional hexagonal phase is reached through melting of the low temperature phase, in which the side chains form crystalline layers similar to those in pure triclinic n-alkanes. The transition from layered to columnar arrangement is consistent with the cylindrical arrangement enabling the accommodation of the expanded melted paraffinic layers.

In a subsequent publication, poly(n-octadecyl glutamate)s (C_{18}) was reported to exhibit a nematic phase below the columnar temperature range[94].

From the comparison of hexagonal X-ray spacings and macroscopic densities, Watanabe *et al.*[92] have suggested that two intertwined chains form a single column both in the case of cellulose tri-n-alkanoates[93] and in poly(n-alkyl glutamate)s with long side chains ($10<n<18$)[92].

A number of rigid aromatic backbone polymers with flexible side groups are currently receiving considerable attention. Some of them, notably polyamides of the type where $R_2=OC_nH_{2n+1}$ and R_1 is either H or C_nH_{2n+1}, display what has been described as a rectangular or oblique lattice of boards (*Figure 5*)[95,96]. The backbone as well as the side chains are conformationally disordered in the present phase, and there is no longitudinal register between the chains.



From the point of view of symmetry, the rectangular variant of this phase would fall in the same category as the rectangular columnar phase in tilted discotics[97,98], or the ribbon phase in some neat soaps[99], both of which form rectangular two-dimensional lattices. However, in the present case, it is not completely clear whether the positional order in both lateral dimensions is truly long range.

Periodic linear macromolecules. In the case of polymers without side branches (group A), like polyethylene, polybutadiene, PTFE or poly(*p*-xylylene), none of the usual reasons for liquid crystal formation can be invoked. There is little doubt that conformational disorder plays an essential role in destroying long range periodicity in the chain direction, reducing the three-dimensional crystalline order to two-dimensional columnar order.

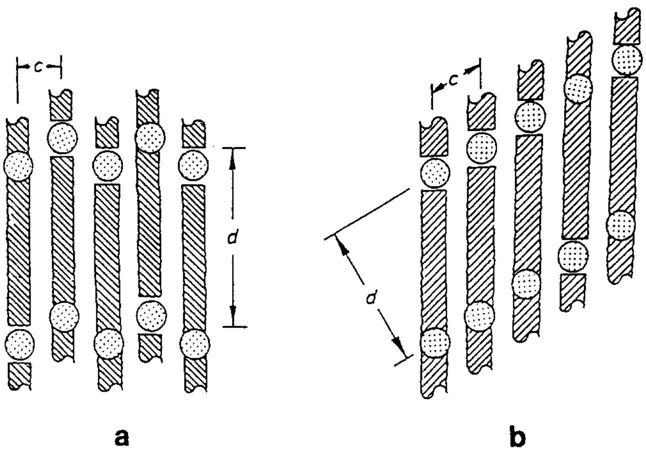


Figure 5 Packing model for the rectangular (a) and the oblique (b) two-dimensional mesophase. View along polymer chain axis. Circles denote rigid polyamide backbones, and shaded rectangles the side groups; *d* is the layer spacing. The unit cell parameters in (a) are *d* and 2*c*. From reference 96. Courtesy of Huthig & Wepf Verlag

Conformational disorder in hexagonal polyethylene was treated by statistical mechanics by Priest[100], by Monte Carlo simulation by Yamamoto[101] and using molecular dynamics simulation by Noid *et al.*[102]. In common to all of these works is confinement of a polymer chain to a more or less rigid cylinder and derivation of average distribution of torsion angles. A different approach to describing the phase behaviour of polyethylene [and also poly(1,4-t-butadiene)] was adopted by Pechold *et al.*[103] who considered conformational disorder in terms of rotational isomers, but assumed their existence in clusters, thus stressing intra- and intermolecular cooperativity.

A molecular mechanics calculation was recently performed for poly(*p*-xylylene)[104] and the results were compared with experimental transition entropies. It was suggested that the main type of conformational disorder in the columnar β_2 phase of this polymer was due only to the rotation of phenylene groups around the molecular axis, rather than to kinked or helical sequences.

In general, co-operative formation of conformational defects, which occupy a small volume and leave the overall chain trajectory unaffected, would allow efficient columnar packing. High entropy is thereby gained with a comparatively small penalty in increased volume, resulting in a low free enthalpy of the mesophase. Thus it may be argued that, while a mesophase with rigid molecules forms because a *disordered* liquid requires an unacceptably *high* excess volume, in flexible systems it can form because the *mesophase* requires an exceptionally *low* excess volume. The idea of a high entropy/low volume mesophase has already been suggested and elaborated to some extent for the case of polyethylene[6,44,105].

Aperiodic linear macromolecules. While a high degree of conformational disorder may render the polymer chain effectively aperiodic, resulting in a two-dimensional rather than a three-dimensional phase, aperiodicity can also be built in chemically. Random placement of small substituents along the main chain has already been shown to promote columnar phase formation in random copolymers of ethylene and propylene[9], ethylene and vinyl chloride[106], tetrafluoroethylene and hexafluoropropylene[16] and VDF and trifluoroethylene[15]. Stereoirregularity offers another route, as manifested by P3FE: the polymer, produced by addition polymerization, is atactic and forms the columnar phase in a wide temperature range, including room temperature[14,107]. While lacking stereoregularity, the polymer usually also

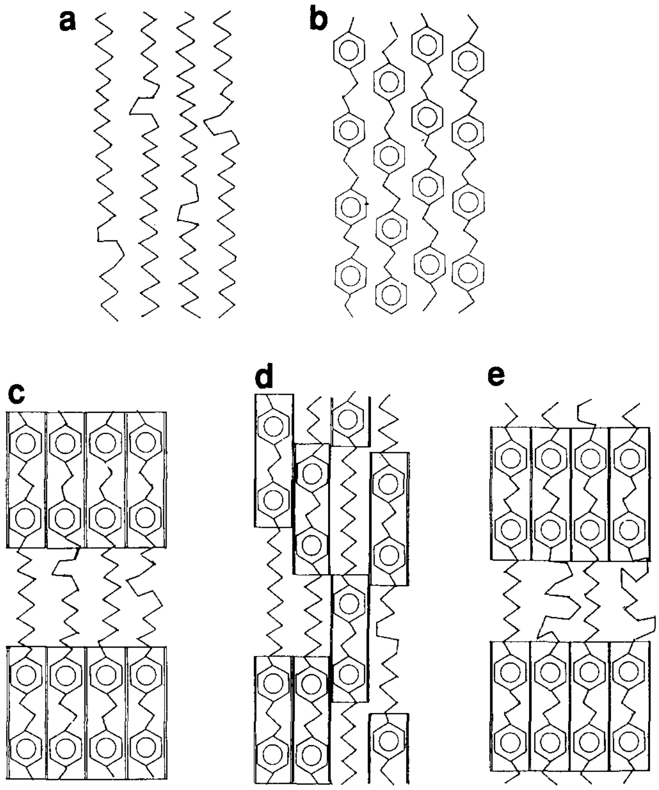


Figure 6 Schematic representation of the hexagonal columnar phases in polyethylene (a) and poly(p-xylylene) (b), of the smectic B phase in BPE-10,12 copolymer with similar spacer lengths (c), and of the high temperature columnar (d) and low temperature smectic B phase (e) in BPE-8,12 copolymer with dissimilar spacer lengths. From reference 108. Courtesy of the American Chemical Society

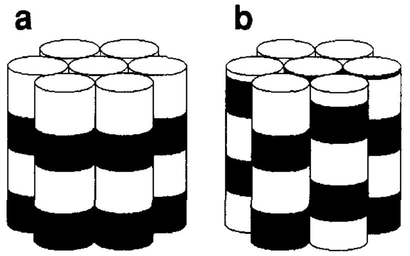
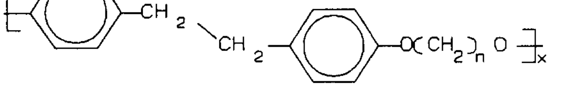


Figure 7 Schematic representation of the three-dimensionally ordered smectic B (crystal B) (a) and two-dimensionally ordered hexagonal columnar phase (b) in BPE[108] and some other[109] segmented copolymers. The black and white segments represent, respectively, the more flexible 'spacers' and the less flexible 'mesogens'

contains a high proportion of head-to-head/tail-to-tail defects. Both types of constitutional defects, while preventing true crystallization, are nevertheless tolerated by the columnar lattice. Such tolerance has been attributed to the similarity of the van der Waals radii of hydrogen and fluorine[84,85,107].

Hexagonal columnar phase has recently been found in a study of the thermotropic behaviour of random main-chain copolymers. These were polyethers based on BPE and alkyl spacers of variable length in the main chain[108].



Whereas BPE homopolymers ($m=n$) are not mesogenic, random copolymers with $m \neq n$ (denoted BPE-m,n) exhibit either a smectic B phase (e.g. copolymer BPE-10,12) or a low temperature smectic B and a high temperature hexagonal columnar phase (e.g. copolymer BPE-8,12). The smectic B is in this case, in fact, three-dimensionally ordered (crystal B type, see *Table 2*).

BPE polymers can, in the first approximation, be considered as copolymers of poly(p-xylylene) and polyethylene (neglecting the difference between ether and methylene groups, see *Figure 6*). Since both the latter polymers exhibit the hexagonal phase, it is not surprising to find such a phase in their 'copolymer'. However, a comparatively large difference in comonomer spacer lengths, $-O(CH_2)_8O-$ *versus* $-O(CH_2)_{12}O-$, is required to depress the smectic B–columnar transition temperature below that of the columnar–isotropic transition (polymer BPE-8,12, see *Figures 6d* and *e*). When the difference in spacers is small, as in BPE-10,12, both spacers can easily be accommodated within the smectic B phase, without the loss of LRO along the chain direction.

The transition from the columnar to smectic (crystal) B phase in BPE-8,12 seems to be a particularly simple example of a two- to three-dimensional phase transition: longitudinal LRO is established as a weak but sharp first-order transition, leaving the lateral (in-plane) order practically unaffected[108]. The two phases are schematically represented in *Figure 7*.

With the understanding of the principles of columnar ordering gained by the above studies, new column-forming polymers can now be designed deliberately. A new series of main chain aperiodic polymers has already been synthesized which not only shows the columnar phase, but for the first time, it also exhibits the nematic phase[109].

CONCLUSIONS

By applying the established criteria for classification of states of condensed matter based on dimensionality of positional and orientational LRO, it is shown that a large number of high temperature polymeric phases, mostly with hexagonal symmetry, are best described as columnar liquid crystals. As with discotic low molar mass compounds and some disc-containing polymers, the above phases comprise hexagonally packed columns with lateral long range positional order, but with only short range order along the columns. Among thermotropic systems these columnar phases are unique in that the molecular long dimension lies along the column axis and in that, most often, the molecules are highly flexible. Moreover, the absence of both rigid mesogenic groups and amphiphilic character from many of the macromolecules concerned, makes the polymeric columnar phase unique within the whole liquid crystal field.

Some apparently two-dimensionally ordered 'board-like' phases in rigid backbone polymers with flexible side chains may also be described as columnar, but with rectangular or oblique rather than hexagonal symmetry.

Furthermore, since it has been proposed previously that most of the two-dimensional liquid crystal phases considered here belong to condis crystals, the classification which divides all mesophases into plastic crystals, condis crystals and liquid crystals, is critically assessed. It is suggested that the term 'condis crystals' be limited to disordered crystals (three-dimensional) where lattice symmetry is increased as a result of conformational disorder.

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