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Liquid crystallinity in linear, helical, columnar supramolecular polymers

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Liquid crystallinity is an important aspect of self-assembly processes in molecular and supramolecular structures of either synthetic or biological origin. Liquid crystallinity in supramolecular polymers (SPs) is controlled by the interplay between classical orientational parameters such as excluded volume, and growth parameters such as contact interactions between self-assembling unimers. A critical analysis of literature data supports the occurrence of the following modes in which liquid crystallinity is expressed by SPs. (1) Liquid crystallinity totally uncoupled to growth (case exhibited by closed SPs, and by discotic unimers characterized by weak binding constants, *K*); (2) liquid crystallinity uncoupled but hierarchically related to growth (case exhibited by open SPs characterized by strong *K*); (3) liquid crystallinity coupled to growth (case exhibited by rigid SPs characterized by intermediate values of *K*). The behaviour of linear, columnar, helical SPs in both lyotropic and thermotropic phases conforms to this description. Important implications and further theoretical analysis of the growth-coupled-to-orientation mechanism await further investigation.

1. Introduction

Excluded volume effects controlling mesophase formation by rod-like and disk-like particles (figure 1) need to be related to the occurrence of intra- and inter-particle association in the case of supramolecular polymers (SPs). For example, the author has compared the expected behaviour for molecularly dispersed rod-like polymers with that for closed and for open SPs [1]. The latter are characterized by a coupling between the hard/soft interactions stabilizing the mesophase and the contact forces (i.e. binding constants) stabilizing the supramolecular assembly [2–5]. The behaviour of closed SPs (when *all* recognition sites are saturated in the isotropic phase) is by contrast indistinguishable from that of molecular liquid crystals.

Following on from this emphasis on the importance of the assembling power of the open supramolecular liquid crystal (SLC), several authors have suggested an enhancement of growth associated with the formation of a mesophase for a variety of SPs [6]. It transpires that only in a few cases has growth coupled to orientation been adequately documented; in the vast majority of cases no such coupling may occur. In fact, there is a need for experimental and theoretical studies of the open SLC. Difficulties arise from the incorporation of chain flexibility in the coupling between growth and alignment.

Several features exhibited by thermotropic SPs and by discotic molecules and supermolecules also require a detailed description of the coupling between excluded volume effects and contact forces. Thus, a critical analysis of the ways in which liquid crystallinity is manifested in supramolecular systems, supported by experimental data in the literature, is presented here. To this end, it is necessary to summarize the salient features of growth mechanisms responsible for the supramolecular polymerization of various types of SPs [7]. Multistage open association (MSOA) is the basic isodesmic polymerization occurring when contact forces holding all unimers are characterized by a single association constant *K*. The degree of supramolecular polymerization (DP) of linear or columnar SPs increases with concentration up to the maximum value ($\sim K^{1/2}$) in the bulk phase [8]. Helical growth (HG) is a cooperative mechanism expected, for example, when binding of a few unimers promotes a stronger binding of successive unimers ($K_h > K$) along a helical pattern. A critical concentration C^* ($\sim K_h^{-1}$) marks the onset of cooperativity [9]. In the case of the open SLC mechanism, growth occurs simultaneously with the formation of nematic order at a critical concentration C^i, and is significantly slowed when the persistent length of the assembly formed is attained [2–5].

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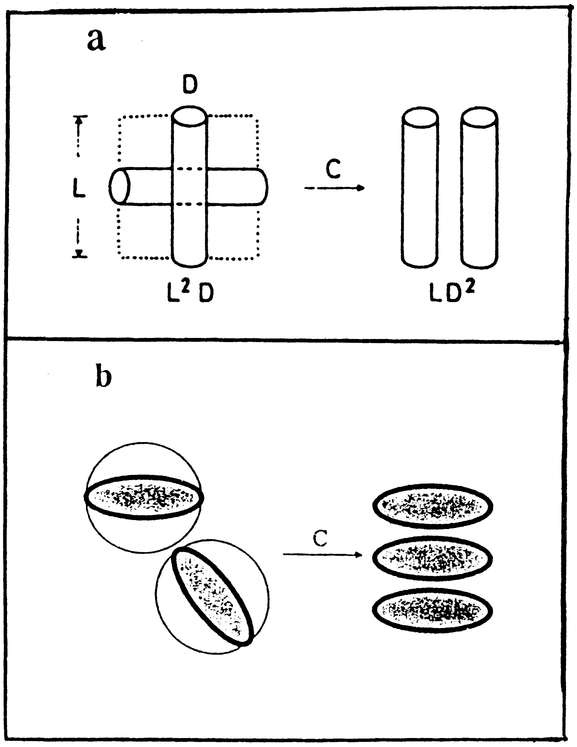


Figure 1. Excluded volume effects. A decrease of free volume favours the formation of parallel assemblies of (*a*) rods and (*b*) columnar assemblies of disks, upon increasing unimer concentration.

2. Liquid crystallinity for molecular and for closed SPs

In the case of a truly closed SLC, the sites are internally compensated and no further growth occurs during or following mesophase formation. Among such examples are DNA and some synthetic polymers. Mesophase formation by DNA [10] was adequately described by the virial and by the lattice theory of molecular liquid crystals [11, 12]. Poly(*p*-benzamide)(PBA) in *N*,*N*-dimethylacetamide/LiCl isotropic or nematic solutions occurred as an assembly of seven PBA molecules with a side-by-side shift of one quarter the molecular length. In this case, even the axial ratio of the assembly (~ 104) was indistinguishable from the axial ratio (~ 100) of molecularly dispersed PBA [13].

3. Liquid crystallinity uncoupled to growth

A new situation occurs if strong growth, due to MSOA or HG in isotropic solutions, has produced at $C < C^{\mathrm{i}}$ a worm-like chain with a length comparable to or exceeding the persistence length. In this case no sudden growth due to the open SLC occurs at the critical concentration, even though growth continues at $C > C^{\mathrm{i}}$ driven by the MSOA or HG mechanism. The case of actin (table 1, No. 1) conforms to this behaviour [9]. In fact, the lowest critical concentration for the appearance of the mesophase reported by Furukawa *et al.* [14] was $\sim 2\,\mathrm{mg\,ml^{-1}}$ for a gelsolin-terminated filament length of $\sim 5\,\mu\mathrm{m}$ (DP ~ 1780). However, Janmey *et al.* were able to grow filaments with a larger length at a concentration of $\sim 0.04\,\mathrm{mg\,ml^{-1}}$ suggesting that actin grows to a length comparable to the persistence length in isotropic solutions ($C^* < C^{\mathrm{i}}$) [15*a*]. Recent data supporting a broad LC transition for actin do not conflict with the present description [15*b*].

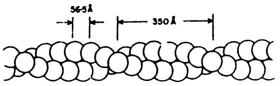
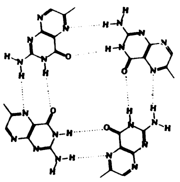
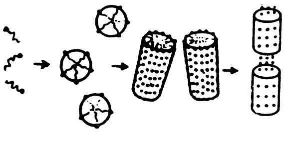
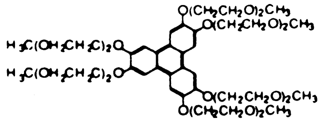
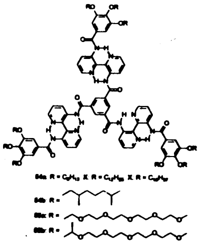
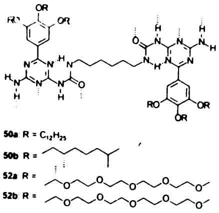
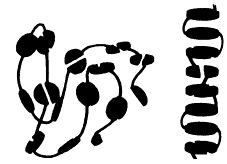
There are other instances of synthetic SPs and fibrous proteins for which growth probably precedes the formation of the mesophase, although a definite conclusion needs additional verification. In the case of microtubules, a synchronous occurrence of growth and liquid crystallinity was reported by Hitt *et al.* [16]. These experiments do not, however, support a coupling between growth and alignment since they were carried out at a tubulin concentration ($15\,\mathrm{mg\,ml^{-1}}$) larger than either the critical concentration at which the helix nucleates or the mesophase appears. In the case of silk, fibroin unimers self-assemble into rodlike particles forming a mesophase upon increasing concentration [17]. However, conformational changes accompanying the transformation are still being investigated [18].

In the case of actin, growth and mesophase formation should be regarded as uncoupled but *hierarchically related* since the liquid crystallinity arises as a consequence of a preassembling step in isotropic solutions. Cases of growth totally uncoupled to liquid crystallinity also exist. One example is the tetrameric H-bonded supermolecule of folic acid (table 1, No. 2) for which the DP was determined by Gottarelli and cowokers using SANS [19]. Their data, plotted in figure 2, show a continuous increase of the number of stacked tetramers with concentration, unperturbed by the occurrence of the mesophase. The DP remains extremely low suggesting that the intensity of contact forces or rigidity do not, in this case, allow cooperative growth due to either the SLC or the HG mechanism. The occurrence of the mesophase may therefore be attributed to the large excluded volume of the disks, cf. figure 1(*b*) and §5. Similar behaviour was reported by Ben-Shaul *et al.* [20].

4. Liquid crystallinity coupled to growth

The most stringent verification of the open SLC model is the demonstration of a sudden increase of polymerization when the nematic phase appears. Supporting data regarding the rigidity (persistence length) of the assembly are needed. Systems for which growth coupled to orientation was adequately

Table 1. Linear, columnar and helical SPs in isotropic (I) and anisotropic (A) solutions. MSOA = multisage open association, HG = helical growth, SLC = supramolecular liquid crystal.

	Polymer/complex	Mech.	Phase	DP	Ref.
1		HG	I	→4000	[9]
2		MSOA	I/A	→20	[19]
3		SLC	A	→1000	[3]
4		SLC	A	→—	[21]
5	 	HG	I/A	→1000	[35]
6	 	HG	I/A	→100	[36]

documented are the formation of linear micelles [3, 5], the columnar stacking of a discotic amphiphile [21], and the polymerization of sickle cell hemoglobin [22, 23].

In the case of micelles (table 1, No. 3), Odijk has critically reviewed data supporting their linear polymerization [2, 3]. Upon increasing surfactant concentration the following hierarchical sequence is exhibited: dispersed molecule→spherical micelles→end-cupped micelles→linear growth + nematic. The broad features of the predicted phase diagram are verified, although the critical concentration appears smaller than predicted [5, 24]. Persistence length data for several

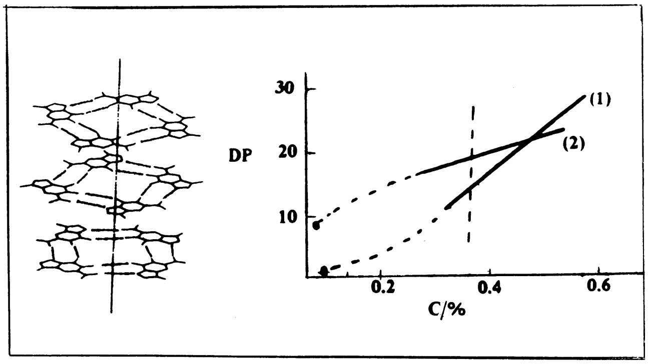


Figure 2. Variation of the number of stacked tetrameric disks (cf. table 1, No. 2) with folate concentration in pure water (1) and 1M NaCl (2) at 30°C. The vertical broken line marks the I→H transition (plotted using data from [19]).

Table 2. Persistence length for supramolecular polymers.

System	$q/\mu m$	q/D	Ref.
DNA/0.2M NaCl	5.4×10^{-2}	50	[30]
Dimethyleylamine oxide/ $H_2O+10^{-2}M$ NaCl	→1.7	280	[31]
Actin/phalloidin-stabilized + buffer	→177	3500	[32]
Microtubules/taxol-stabilized + buffer	→5200	170000	[32]

surfactants support a large linear growth even though considerable scattering (from 0.02 to 10 μm) is exhibited [2] (cf. table 2).

A discotic amphiphile based on triphenylene with polar sidechains (2,3,6,7,10,11-hexa-(1,4,7-trioxaocetyl)-triphenylene in D_2O, table 1, No. 4) was investigated by Boden and coworkers [21, 25]. Large columnar stacks were formed at a volume fraction $v \sim 20\%$ (rt) simultaneously with the isotropic→nematic transition. The nematic phase was stable up to $v \sim 40\%$, when the hexagonal columnar phase appeared, to be followed at $v > \sim 60\%$ by higher order phases. The experimental data were remarkably in line with predictions of the growth-coupled-to-orientation theory as elaborated by Hentschke [4], but no persistence length data are available. The nematic phase is promoted by a favourable balance of contact forces, flexural rigidity and excluded volume, and evolves into the hexagonal columnar phase due to its better packing efficiency as compared with the nematic phase. The sequence of phases, representing a hierarchical evolution of the assembly process from nanoscale to mesoscale dimensions, can thus be summarized: dispersed disks (I) → growth + nematic (N) → hexagonal (H) → higher order phases. Osmotic pressure vs. concentration data for normal (non-aggregating) and sickle cell haemoglobin reported by Hentschke and Herzfeld [22] support the simultaneous onset of linear growth and alignment at ~20% concentration. The linear assembly attained length in the μm range.

Among the features of the SLC mechanisms that await more detailed investigation, there is a need for a quantitative assessment of the range of contact forces and flexural rigidity that allow stabilization of the nematic phase. Systems with varying numbers of interacting sites and persistence lengths need to be investigated. In fact, there are examples in which the nematic phase is not observed (e.g. some surfactants and block copolymer micelles [26, 27]), and it is not clear if the effect is due to the delicate balance of the two parameters required by theory [5]. The growth–alignment coupling could be more conveniently studied in dilute solution if it were possible to use an external field to mimic the LC ordering. Other interesting features that need additional investigation include the possible coalescence of unimers to form a continuous filament (as suggested by simulation studies on the growth of end-capped block copolymer micelles [28]), and the assembly of supramolecular helices simultaneously with nematic orientation (an alternative to the HG mechanism in isotropic solutions).

Values of persistence length have been determined for only a few supramolecular assemblies and reveal a much larger rigidity than reported for molecular polymers [29]. Table 2 includes data for elongated assemblies having different shapes (linear, helical, tubular). The value for DNA [30] was determined by light scattering using the classical equation for unperturbed wormlike chains. For micelles, light scattering data for the non-ionic surfactant dimethyloleylamine oxide are reported [31 *a*]. The study revealed the formation of worm-like micelles having an aggregation number affected by the concentration of added NaCl. A better account of polydispersity was discussed [31 *b*]. Alternative determinations for other types of micelles provided values of q ranging from 0.02 to 10 μm [2]. The q values for cytoskeleton assemblies were assessed from their flexural rigidity measured from thermally driven fluctuations in shape [32] or from fluctuations of the end-to-end distance. The persistence length of microtubules (reaching 5.2 mm!) is larger than the length of the samples used for its determination and of microtubules found in cells [32]. The tubular shape, achieved by lateral association of 13 to 16 protofilaments composed of linear sequences of α- and β-tubulin molecules, appears to be a most efficient way to maximize the bending stiffness.

5. Discotic SPs

Some peculiarities need to be considered when the LC behaviour expected for discotics interacting by excluded volume effects is coupled to the occurrence of contact forces and supramolecular polymerization. Simulation studies support the formation of nematic (N_D) and columnar phases in solutions of thin non-associating disks characterized by thickness/diameter (*L*/*D*) ratios between 0 and 0.1 [33]. The *L*/*D* ratio of typical self-assembling discotics (e.g. those in table 1) is in the order of 0.1. Such a large asymmetry should lead to the formation of mesophases, even in the absence of contact forces between their surfaces.

The superposition of contact forces is expected to produce alterations in the asymmetry of particles and in the rotation of individual disks. The disks will in fact begin to associate even in the isotropic solution, and the corresponding increase of thickness will cause the *L*/*D* ratio to increase. Moreover, in the absence of contact forces, non-associated disks undergo free rotation around the axis of a columnar stack in the mesophase. If contact forces also occur, a coordination in the free rotation of disks will appear.

In the context of the present discussion it is useful to consider the superposition of excluded volume effects and contact forces in the limit of strong and weak association constants. For large association constants K, elongated columnar assemblies ($L/D > 1$) are expected, with individual disks separated by short separation distances and no longer freely rotating. The net effect of association is a reduction of the anisotropy of single disks and a suppression of the N_D phase with an evolution toward the predicted cubatic phase ($L/D = 1$) [34] and rodlike ($L/D > 1$) behaviour. In the case of weak equilibrium constants, when only short oligomers are expected, the formation of the N_D phase should simply be shifted to a larger critical concentration due to the modest increase of particle thickness.

This subtle way in which the geometrical asymmetry of the disks is expected to couple with contact forces for the formation of LC phases is supported by data presented in table 1. In cases of strong association constants, discotic columns have been shown to form via the HG mechanism in isotropic solutions [6*a*, 35, 36] (table 1, Nos. 5, 6). Liquid crystalline behaviour eventually develops at higher concentrations, promoted by the excluded volume of long rigid particles, uncoupled but hierarchically related to growth as discussed in §3.

Cases in which equilibrium constants are rather weak are exemplified by folic acid tetramers (table 1, No. 2, cf. §3) showing complete uncoupling between growth and liquid crystallinity. The data in figure 2 show no cooperative growth producing large (> 1) axial ratios. The mesophase appears at $\sim 40\%$ concentration and DP is ~ 10 when the axial ratio is still < 1.

Finally, in the case of a favourable combination of moderate association constants and flexural rigidity (e.g. table 1, No. 4), the coupling of growth and liquid crystallinity again produces a suppression of the N_D phase due to a large increase of the *L*/*D* ratio.

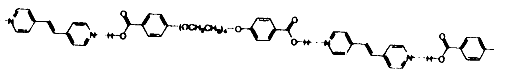
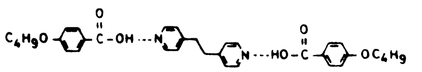
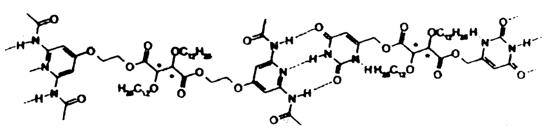
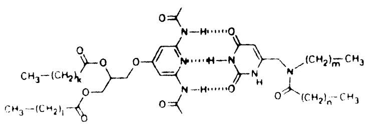
6. Thermotropic SPs

Often the formation of supramolecular dimers, or low DP oligomers, between similar or dissimilar components is accompanied by the formation of a liquid crystalline phase. For instance, hydroxypyridine dimers [37] or H-bonded complexes between adenine and thymine [38] are capable of forming liquid crystals. Non-mesogenic pyridine and carboxylic acid derivatives have also been shown to develop liquid crystallinity upon complexation [39]. Complexation at the side chain of a non-mesogenic, flexible polymer may also result in the formation of mesophases [40, 41]. The behaviour of side chain thermotropic SPs will not be considered here due to the lack of growth when monofunctional binding sites are involved. Relevant to the present context is the behaviour of main chain SPs. It is important however to specify if the conformation of the main chain is described by the wormlike or by the segmented model (short rigid segments separated by flexible spacers) [11, 12].

The linear segmented assemblies based on a dipyridyl and a diacid originally reported by Griffin and coworkers (table 3, No. 7) exhibit a thermotropic nematic phase [42]. Liquid crystallinity in similar segmented chains is a reflection of the soft anisotropic interaction occurring for the low molar mass mesogens incorporated in the main chain [43, 44]. In fact, both a large geometrical asymmetry and persistence length are hindered by the flexible spacers, and the segmental order parameter has been shown to be greatly reduced at the δ-position from the rigid unit [44]. For this class of system, the occurrence of polymerization could be evidenced by higher transition temperatures with respect to the corresponding low molar mass mesogen [44]. It is difficult, however, to assess quantitatively the value of DP starting from the increased T_{NI}, particularly when, as in the case of polymer No. 7 and the dipyridyl complexed with two monofunctional acids No. 8 [42], comparable T_{NI} temperatures (respectively 180° and 178.5°C) are exhibited. The actual DP of polymer No. 7 may be evaluated using the relationship $\mathrm{DP} \sim K^{1/2}$ derived for the MSOA mechanism which, on the basis of a binding constant in the order of $500\,\mathrm{M}^{-1}$, yields a value in the order of 20.

In principle, assembly in thermotropic systems should be enhanced by the formation of the nematic

Table 3. Linear, columnar and helical SPs in thermotropic (T) bulk phase.

	Polymer/complex	Mech.	Phase	DP	Ref.
7		MSOA	T	20[a]	[42]
8		—	T	—	[42]
9		MSOA (HG)	T	100[a]	[45]
10		—	T	—	[46]

[a]Theoretical estimate from MSOA.

phase, just as in the case of the lyotropic systems Nos. 3 and 4 in table 1. Bladon and Griffin have indeed theoretically shown that growth is expected for a worm-like chain forming a nematic phase stabilized by soft interactions of the Maier–Saupe type [42]. It is likely that the segmented nature of polymer No. 7 prevents the occurrence of growth-coupled-to-orientation. A recent review describing other examples of thermotropic SPs based on a single H-bond scheme, offers no evidence for the occurrence of a considerable DP or a correlation between liquid crystallinity and growth [6 *c*].

Thermotropic SPs based on unimers with multiple H-bonding also reveal a difficulty in assessing the DP and a detailed growth mechanism. In truly pioneering work, Lehn and coworkers prepared polymer No. 9 (table 3) from bifunctional tartaric acid derivatives (D,L or meso M) terminated with either two 2,6-diaminopyridine (P) or two uracil (U) derivatives [45]. The P–U bond is based upon a triple H-bond scheme with the DAD–ADA arrangement. All the polymers exhibited thermotropic mesophases in the range 25–250°C. X-ray and TEM data revealed a triple helical structure and fibre-forming properties for the chiral polymer (LP_2, LU_2) in contrast to the achiral sample (MP_2, MU_2) that exhibited individual chains in a zig-zag conformation and other features typical of a flexible polymer. The qualitative interpretation currently favoured is that of growth developing simultaneously with liquid crystallinity in the undiluted state according to the open SLC mechanism. No independent support for this interpretation however exists.

An alternative assessment of DP and of the growth mechanism can therefore be suggested for these chiral and achiral polymers. In view of the flexibility of a single chain of polymer No. 9 (table 3) it is unlikely that the open SLC mechanism might have been operative. On the other hand, the circumstantial evidence reported by Lehn and coworkers supports the possibility that the triple helix of the chiral polymer formed even in the presence of solvent. Therefore, it is possible to suggest that the triple helix was nucleated by the HG mechanism, whereas liquid crystallinity is simply a reflection of the excluded volume of the rigid assembly. The expected DP of the chiral polymer should be larger than the value predicted by the MSOA mechanism. The latter, estimated assuming an equilibrium constant for the DAD–ADA array in the order of $10^4\,M^{-1}$, is ~ 100.

In the case of the achiral polymer (MP_2, MU_2), growth by the open SLC mechanism is again precluded by single chain flexibility. Moreover, even growth due to the HG mechanism is ruled out since no cooperative helix formation was observed. The DP should therefore be close to the value predicted by the MSOA mechanism. The origin of liquid crystallinity should be related to intrinsic characteristics of the P–U assembly such as soft anisotropic interactions, or the ability to form disk-like assemblies such as those documented for the compound No. 10 described next.

The monofunctional P–U complex No. 10 (table 3) has been shown to form disk-like unimers that can self-assemble into columns displaying thermotropic behaviour. Each disk, containing two units of complex No. 10, has a thickness/diameter ratio of ~ 0.1 [46]. The formation of columnar mesophases by similar discotic supermolecules was described in §5 when three different self-assembly modes were considered. These correspond to situations in which liquid crystallinity and growth are hierarchically related, coupled, or totally uncoupled. Lack of data on the equilibrium constants, or DP, prevents a definite assessment of the assembling mechanism for discotics based on complex No. 10.

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