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A. Ciferri [a] & W. R. Krigbaum [b]
[a] Centro Studi Macromolecole, Istituto Chimica Industriale, University of Genoa, Genoa, Italy
[b] Gross Chemical Laboratory, Duke University, Durham, North, Carolina, 27706, U.S.A.
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Self-Assembly of Natural Polymers Via Liquid Crystalline Phases

A. CIFERRI

Centro Studi Macromolecole, Istituto Chimica Industriale, University of Genoa, Genoa, Italy.

and

W. R. KRIGBAUM

Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706 U.S.A.

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There are numerous examples of biological materials in which the supermolecular organization of a solid resembles that of a liquid crystal. Bouligand has proposed that a liquid crystalline phase may be the precursor of such solids, but without offering any detailed mechanism for this type of transition.

Examination of the various equilibria involving a polymer in the crystalline state, and its isotropic and anisotropic solutions, suggests a possible mechanism. There may be a region in the phase diagram in which the isotropic phase is unsaturated, while the conjugate anisotropic phase is supersaturated. If the solubility curve of crystalline polymer in the isotropic phase intersects the "wide" portion of the biphasic region, a very dilute isotropic solution will be in equilibrium with a concentrated and supersaturated anisotropic phase which must crystallize. An open system incorporating these features would be capable of the continuous production of a crystalline polymer having the morphological features of the liquid crystalline phase.

The exquisitely detailed structural organization of materials of biological origin has led to considerable theoretical interest in processes which might transform an initially homogeneous system into one in which the component parts are differentiated and organized spatially. A seminal theoretical paper by Turing[1] investigated possible chemical bases for morphogenesis, and the theory has subsequently been generalized and more fully developed in the thermodynamic treatment of fluctuations in irreversible processes (see, for example, Glansdorff and Prigogine[2]). In this paper we restrict our attention to the subset of biological materials in which the supermolecular organization of

a solid resembles that of a liquid crystal at rest, or under the influence of an external field.

We begin by citing some examples of biological solids which fall into this class. A layer of cuticle consists of a planar, uniaxial arrangement of chitin fibrils. In certain insects the direction of preferred orientation in successive layers varies in a regular, periodic manner, tracing out a helix.[3] This structure is, quite evidently, very similar to that of a cholesteric liquid crystal. Furthermore, the similarity extends to include the remarkable optical properties; *i.e.*, the ability to selectively reflect incident light in a narrow band of wavelengths as circularly polarized light. This was observed for certain insect cuticles by Michelson as early as 1911,[4] and the similarity of this behavior to that of cholesteric liquid crystals was pointed out by Gaubert,[5] Mattieu and Farragi,[6] and by Robinson.[7] Turning to another example, the tropocollagen helices of the collagen fiber are aligned parallel to the fiber axis, with a staggered end overlap region 280Å in length.[8] The parallel arrangement of units is reminiscent of the arrangement of molecules in a nematic liquid crystalline phase. The fibrils in the core of the cellulose fiber are also well aligned parallel to the fiber axis, while those in the outer wall follow a rather flat helical pattern about the fiber axis.[9] By contrast, polymerization of fibrinogen molecules forms an open network structure of fibrils in the fibrin clot, the overall structure being isotropic.[10]

Bouligand[11] has proposed, as an explanation of the organization observed in the types of anisotropic solids mentioned above, the existence of a liquid crystal phase prior to solidification. Support for his proposal is provided by the observation that the fundamental unit in these structures, whether a molecule or fibril, has a high axial ratio, which is a requirement for the formation of a lyotropic liquid crystalline phase. However, there have been no detailed suggestions concerning how the spatial arrangement characteristic of the liquid crystalline phase could be retained during solidification. Our objective is to provide a possible mechanism for this process.

Solidification with preservation of a preexisting structure may be promoted through formation of a gel,[2] a glass,[13-14] or by the introduction of chemical crosslinks.[15] However, in the majority of cases solidification involves crystallization. One can cite numerous examples in which the organization of a polymeric liquid crystal is retained following crystallization. Samulski and Tobolsky[16] found that the cholesteric focal conic (fingerprint) texture of lyotropic poly(γ-benzyl-L-glutamate) was still observable in the crystalline films formed by solvent evaporation. The outstanding properties of ultra-high modulus aromatic polyamides[17] arise from retention of the organization present in the anisotropic spinning solutions. In this case the nematic domains are easily aligned along the fiber axis by a small tension applied to the liquid

filament.[18] Work in this laboratory[19] has demonstrated that a Williams hydrodynamic flow pattern, which was induced in the nematic phase of a thermotropic polymer by application of a d.c. field, was still clearly evident following crystallization of the sample. Hence, in contrast to low molecular weight mesogens, in which crystallization is accompanied by a thorough structural reorganization, crystallization with conservation of a preexisting structure appears to be quite common among polymeric mesophases.[20] However, in all of these cases the liquid crystalline phase is either a bulk polymer in the molten state, or a rather concentrated solution. Hence, retention of structure during solidification can be attributed to long relaxation times characteristic of polymeric systems at high concentration. By contrast to these examples, a crystalline solid having a morphology resembling that of a mesophase often forms in living organisms at extremely low polymer concentrations. In such a case the relaxation time in the liquid crystalline phase does not appear to offer an adequate explanation.

The transformation from anisotropic liquid to crystalline solid which is of interest for biological materials involves lyotropic systems of rather rigid and elongated molecules. The liquid-liquid equilibrium involving the isotropic and anisotropic phases was first treated by Onsager[21] and Isihara.[22] A recent paper by Flory and Ronca[23] is specifically concerned with low molecular weight mesogens, while the earlier lattice model treatment of Flory,[24] which treated macromolecules of rodlike shape, was the first to predict the phase diagram over the full concentration range. The prediction of this latter treatment for rods having an axial ratio of 100 is illustrated by the heavier curves in Figure 1. In this plot the volume fraction of polymer, v_2, is shown as a function of the interaction parameter χ_1. The latter is given by:

$$\chi_1 = 1/2 - \psi_1 + \psi_1\theta/T \tag{1}$$

where ψ_1 is an entrophy parameter and θ the Flory theta temperature. The interaction parameter, used in place of temperature, is a measure of solvent power (which increases as χ_1 decreases). The three regions in the liquid-liquid portion of the phase diagram mark the existence of the anisotropic phase (A), the isotropic phase (I), and a binary liquid phase ($A + I$) in which both anisotropic and isotropic phases coexist. Numerical calculations indicate that when $\chi_1 = 0$, the critical volume fraction of rods required for separation of an anistropic phase is given approximately by $v_2 \simeq 8/x$, where x is the axial ratio of the rod.

Next, we consider the equilibria involving a crystalline phase. The equilibrium between the isotropic solution and the crystal is described by the classical result obtained from the Flory–Huggins treatment of macromolecules of arbitrary shape and flexibility:[25]

$$\frac{1}{T_M} - \frac{1}{T_M^\circ} = \frac{Rx}{\Delta H_f}\left[\left(1 - \frac{1}{x}\right)v_1 - \frac{1}{x}\ln v_2 - \chi_1 v_1^2\right] \tag{2}$$

Here T_M is the melting temperature of the polymer in equilibrium with an isotropic solution in which the volume fraction of polymer and solvent are v_2 and v_1, respectively, T_M° is the thermodynamic melting temperature of the pure polymer, and $(\Delta H_f/x)$ is the heat of fusion per mole of polymer segments, each occupying the same volume as a solvent molecule. Of course, one can equally well regard v_2 as the volume fraction of polymer in the saturated, isotropic solution at temperature T_M. A relation applicable to the equilibrium between crystalline polymer and an anisotropic liquid phase was previously obtained by the authors,[26] using Flory's expression for the activity of rod-like particles in an anisotropic phase:

$$\frac{1}{T_M} - \frac{1}{T_M^{\circ\prime}} = \left(\frac{Rx}{\Delta H_f'}\right)\left\{-\frac{1}{x}\left[\ln\left(\frac{v_2}{x}\right) + (y-1)v_2 + 2 - \ln y^2\right] - \chi_1 v_1^2\right\} \tag{3}$$

Here $T_M^\circ{}'$ and $\Delta H_f'/x$ are the analogs of the parameters introduced above, but for the equilibrium between a crystalline polymer and its anisotropic melt, and y is a parameter appearing in the treatment of Flory which measures the disorientation of the rods in the anisotropic phase. It is given by:[24]

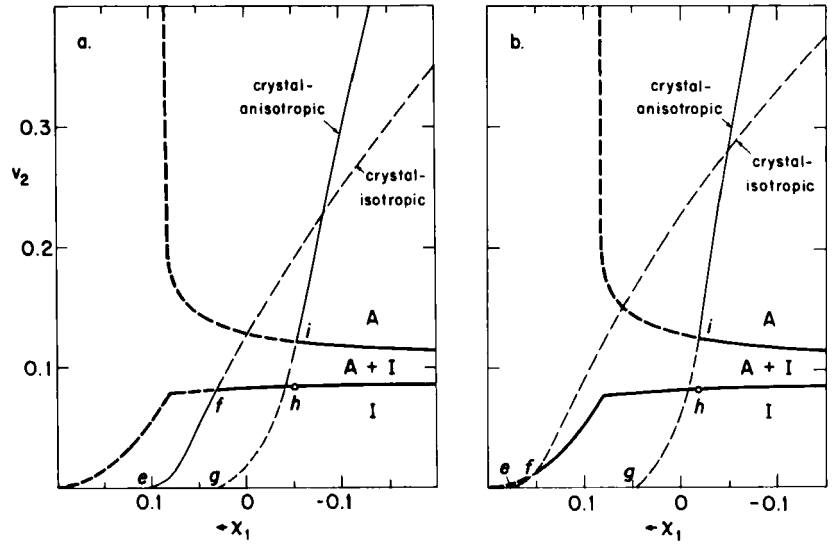

FIGURE 1 Superposition of liquid-liquid (Flory) and crystal-liquid phase diagrams for a lyotropic nematogen having larger (left) or smaller (right) values of T_M° and ΔH_f. Dashed lines indicate regions of metastability.

$$y = -2/[1 - \nu_2(1 - y/x)] \quad (4)$$

The solubilities predicted according to Eq. (2) and (3) are illustrated by the lighter dashed and full curves in Figure 1.

Let us first consider the case of a polymer having a relatively high melting temperature and large heat of fusion, as illustrated in Figure 1a. The parameters used for this calculation are $x = 100$, $T_M^\circ = 800$K, $T_M^\circ = 400$ K, $(\Delta H_f/x) = 900$ cal./mole, $(\Delta H_f'/x) = 400$ cal./mole, $\psi_1 = 2.50$ and $\theta = 250$K. The solubility curve for the isotropic solution begins at point *e* and continues to point *f*. Dashed curves represent portions of the theoretical diagram which are inaccessible due to superposition of the various equilibria.[12] For example, intrusion of the biphasic liquid at point *f* prevents the attainment of a saturated isotropic solution at points beyond *f*, so the remainder of this solubility curve is dashed. The predicted solubility curve for the anisotropic phase begins at point *g*, but this curve first crosses the liquid-liquid biphasic region at point *i*. Hence, a saturated anisotropic solution is only attainable at concentrations corresponding to point *i* and above. Accordingly, the portion of this curve from *g* to *i* is shown dashed. The lower portion of the liquid-liquid biphasic region to the left of point *f* lies above the solubility curve of the isotropic solution and cannot represent an equilibrium state, as indicated by the dashed curve in this region. Similarly, the upper boundary of the biphasic region to the left of point *i* represents a non-equilibrium situation with respect to the solubility of the anisotropic phase, and is therefore indicated by a dashed curve.

For χ_1 values between those corresponding to *e* and *f*, stable isotropic solutions may be induced to crystallize by increasing the polymer concentration or reducing the solubility (increasing χ_1). A crystalline phase formed under these conditions could not exhibit mesophase morphology. For χ_1 values to the right of point *i*, a stable anisotropic phase can exist if ν_2 exceeds that of the conjugate anisotropic phase of the binary liquid region. Such a solution may be crystallized by the same procedure described above. The solid might retain some vestiges of the morphology of the anisotropic solution, depending upon the relaxation time of the molecules in the anisotropic phase. In biological systems crystallization might be accomplished by dissolution of newly synthesized polymer in the extracellular fluids or by alteration of the ionic strength or composition of this liquid.

Of more interest is the range of χ_1 values between those corresponding to points *f* and *h*. An unusual situation is encountered in that, while (as indicated above) the isotropic solution cannot reach saturation, any attempt to increase ν_2 above the lower boundary of the biphasic region must lead to separation of an anisotropic phase which is metastable with respect to the crystalline solid. Since nucleation of the anisotropic liquid phase should be more rapid than nucleation of the crystalline phase,[27] we may expect a metastable anisotropic

phase to appear, and then to be transformed into a crystalline phase. This would appear to be a very efficient mechanism for recrystallization. Such a system may reach a stationary state, but it cannot exist in thermodynamic equilibrium because the isotropic phase is unsaturated. Indeed, the behavior of this system in the region *f–h* bears some similarity to the models of Lotka[28] and Volterra[29] which exhibit oscillation about a stationary state. The volume fraction required to enter the biphasic region is $v_2 \cong 0.08$ for $x = 100$ and, of course, a still more concentrated solution would be required for crystallization from a single anisotropic phase.

In terms of providing a mechanism for the self-assembly of organized solid biopolymers, the situation depicted in Figure 1a is deficient in two respects. First, the concentration of the anisotropic phase is relatively low, so the relaxation time may not be sufficiently long to preserve the structure of the anisotropic phase in the solid state. Secondly, the polymer concentration required for formation of the conjugate anisotropic phase seems large relative to some of the observations for biopolymers. For example, separation of two liquid phases is observed for tobacco mosaic virus at a concentration of about 2%,[30] while the fibrin clot forms at concentrations below 1%.[10]

A more satisfactory picture emerges if the melting temperature and heat of fusion are smaller, as shown in Figure 1b. For this example, T_M° and $T_M^\circ{}'$ are 700 and 300K, and $(\Delta H_f/x)$ and $(\Delta H_f/x)$ are 600 and 300 cal./mole, respectively, while $\psi_1 = 2.50$ and $\theta = 200$K. Since the crystalline polymer is now more soluble, the solubility curves intercept the χ_1 axis at more positive values. In fact, the solubility curve of the isotropic solution now intersects the lower boundary of the binary liquid phase in the "wide" region. The volume fraction at this intercept is only 0.012, while that of the conjugated anisotropic phase would be near unity. Along the curve *f–h*, but beyond *f*, the isotropic solution cannot become saturated due to the intervening separation of the anisotropic phase, but the latter is metastable and must ultimately crystallize. In brief, this is the efficient recrystallization mode described above. However, in the present case the volume fraction of the metastable anisotropic phase is quite large, so that its morphology would be more likely to be carried over into the solid nucleated in that phase. Biological systems must, of course, be treated thermodynamically as open systems. One can imagine such an open system reaching a stationary state just beyond point *f*, with the rate of freshly synthesized polymer being matched by the crystallization rate of polymer in the metastable anisotropic phase. This provides a mechanism for the continuing accretion of solid polymer having the morphology of its liquid crystal precursor.

In summary, there are several examples of biological structures in which the morphology of the solid resembles that of a liquid crystal. It seems quite likely that, in these cases, the solid phase was nucleated in, and grown from, the

anisotropic liquid phase. Consideration of the various equilibria involving the crystalline polymer and the anisotropic and isotropic solutions indicates the conditions under which such a crystallization may occur. If the solubility curve of the isotropic phase intersects the liquid-liquid portion of the diagram in the "wide" biphasic region, a very low polymer concentration is sufficient to ensure crystallization from a very concentrated anisotropic phase. Under these conditions there would be an excellent opportunity to retain in the crystalline solid the supermolecular arrangement of the metastable anisotropic phase which is its precursor. Incorporation of these features in an open thermodynamic system would permit continuous production of a crystalline polymers having the morphological features of a liquid crystalline phase. These conclusions are in agreement with the less detailed suggestions of Bouligand[11] and Flory.[24]

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