

Properties of Materials and their Molecular Bases. New Approaches towards Understanding Liquid Crystals and Polymers

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ABSTRACT

The fundamental bases of liquid crystals and polymers—both widely employed in, and critically important to, modern society—apparently remain poorly understood. Hence, the need to explore alternative explanations to current paradigms.

Thus, liquid crystals are viewed as partially molten solids that retain a semblance of the order of their crystalline precursors. However, this seems unviable as the long-range order in the resulting mesophase cannot survive at temperatures higher than the melting point of the crystal itself.

In polymers, the non-covalent intermolecular forces are believed to be additively amplified along the length of the macromolecule. However, this ignores the fact that the said forces remain minuscule at the sub-unit level, so a collection of macromolecules would be continually associating and dissociating at each contact point. It is doubtful that this can explain the observed mechanical strength of polymers (leading to the “polythene enigma”).

It is argued herein that liquid crystals arise via the entanglement of long chains and U-shaped moieties in the incipient crystalline melt, a process essentially facilitated by proximity effects in the crystal. Thus, the entanglements are not easily reversed once the proximity effects are lost in the mesophase, which is likely a nanoparticle aggregate possibly composed of quasi-rotaxane and quasi-catenane species. Furthermore, liquid crystals—even those derived from achiral molecules—display optical activity, which is critical to their application in display devices. Although this

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symmetry breaking remains enigmatic, a chiral mechanochemical effect or even parity violation are possible explanations.

In the case of macromolecular association, it is argued that the van der Waals force is inherently strong in enthalpy terms, but is stymied by entropic effects which dominate in the weak forces (generally). However, the entropic effects are possibly “damped” in the macromolecule (although in a subtle manner), so association is much greater than currently estimated. These lead to interesting theoretical insights into enthalpy-entropy relationships in atomic and molecular interactions, a sigmoid relationship possibly being indicated.

Keywords: Catenane; enthalpy-entropy relationships; macromolecule, mechanochemical; mesophase; parity violation; polyethylene; rotaxane; symmetry breaking; van der Waals.

1. INTRODUCTION

Modern technological civilization relies critically on specialty materials—whether metals (including alloys) or polymers or novel functional materials—for its smooth functioning. These materials are almost always the products of sophisticated innovation that undoubtedly defines the cutting edge of technological progress [1]. This leads to the plethora of conveniences that characterize current human existence: modern methods of communication and transport, shelter and health care, etc. Clearly, the high quality and standard of life enjoyed by modern societies would be impossible without a well-founded (and funded) base of materials science!

Thus, a fundamental understanding of the properties of materials is undeniably of paramount importance for further innovation — to effect improvements in existing ones or explore and discover new ones [2-4]. This article deals with two classes of materials of particular importance and concern to chemistry, liquid crystals and polymers. These are indeed exemplars of the application of fundamental chemical principles to the design and discovery of products that have had a quotidian impact on modern life. (Interestingly, both liquid crystals and synthetic polymers share a contemporaneous history, dating back to the turn of the twentieth century.)

Liquid crystals represent an intriguing class of materials that have been apparently robbed of their due fundamental significance, by a blasé approach that focused on their admittedly enormous practical importance [5]. Indeed, as argued below, lurking in this Cinderella story lies a gem of great theoretical import and fascination, offering insights and opportunities seemingly hiding in plain sight! (However, this in no way detracts from the enormity of the scientific achievement that propelled liquid crystals from a

curiosity to a technological work-horse, as a critical component of the digital display devices that enable the routine use of modern electronic gadgetry.) All the same, the current view that liquid crystals retain much of the order of their crystalline precursors seems unviable, thus calling for alternative explanations.

Synthetic polymers, although far more commonplace than liquid crystals, yet pose intriguing theoretical challenges [6]. In fact, polymers in general represent an interesting case wherein the molecular structural theory is apparently manifest in the macroscopic domain, in terms of directly observed mechanical properties. Thus, current explanations are based on the idea that the non-covalent forces between the macromolecular constituents of polymers are additively amplified, thus leading to their characteristic strength, hardness, etc. However, this seems oversimplified, as the said non-covalent forces remain minuscule at the level of the sub-units of the macromolecule.

It is the purpose of this article to deal with the lacunae briefly mentioned above. These, in fact, can be addressed largely within the known conceptual framework of molecular science, although interesting extensions lead to intriguing and fascinating new insights.

2. DISCUSSION

2.1 Liquid Crystals

2.1.1 Current views: The mesophase

The liquid crystalline phase has for long been viewed as consisting of a fluidic mesophase, which essentially retains much of the order of the previous crystalline solid [5,7-14]. Qualitatively, the fluidity corresponds to the loss of the crystalline order, although the order

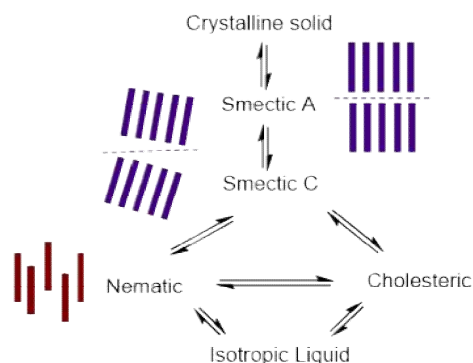


Fig. 1. Cartoon depiction of order as envisaged in the mesophase theory (from ref. 5)

may be retained within sliding sheets (smectic), or in longitudinally aligned dispersion (nematic) models (Fig. 1). The initially discovered cholesteric model implicates the nematic model with a helical twist derived from the chirality of the cholesteryl moiety. The balance between the observed fluidity and the presumed order is believed to be maintained by long range attractive forces between the constituent molecules. Thus, the mesophase—as per the above models—is believed to define an order in between the crystalline solid and the isotropic melt.

However, as has been argued previously [5], there are serious problems with the mesophase theory, essentially for two reasons. Firstly, the weak long-range forces cannot be sustained at temperatures higher than the melting point of the crystal, as the short-range crystalline forces would be far stronger than the putative long-range forces in the mesophase. Just on this basis alone, the mesophase theory seems unviable. (Also, in fact, a random collection of microcrystals cannot yield a mesophase that is uniformly oriented at the molecular level!)

Another problem with the mesophase theory derives from the observation of optical activity in liquid crystals, an intriguing discovery dating back to the earliest days of liquid crystal research [7]. In fact, although the initial studies with the polarizing microscope were performed on cholesteryl benzoate, subsequent studies indicated that liquid crystals derived from achiral molecules also exhibited optical activity. Although the analysis of the results is complicated in many ways, the above mesophase models cannot per se explain the observed optical activity.

Thus, the optical activity apparently arises upon imparting a twist to a nematic liquid crystal. However, the act of mechanical twisting cannot result in molecular level chirality, which would be required for optical activity to be observed. Therefore, the detection of optical activity in liquid crystals may well represent a case of symmetry breaking, which is in some way connected with the formation of the liquid crystalline phase. Hence, the origins of the symmetry breaking can only be clarified if the liquid crystalline phase itself is laid on a sound conceptual foundation.

The essential paradox of the liquid crystalline state lies in the persistence of a metastable state over an extended temperature range: The current paradigm is apparently unable to deal with this key feature. Furthermore, the optical activity exhibited by liquid crystals represents both an application—being the basis of the famed electronic display devices—as also an opportunity for fundamental exploration (*vide infra*).

2.1.2 A model based on molecular entanglements: Quasi-catenanes and rotaxanes

In view of the above lacunae in the mesophase model, it is clearly necessary to look for alternative models that are conceptually viable. An interesting model is based on the possibility of molecular entanglements that occur in the crystalline precursor just prior to its melting (Fig. 2). This is indeed plausible as long-chain moieties are often required for the formation of the liquid crystalline phase (Fig. 3), so the moieties can entangle either among themselves or with other moieties. Other “acceptor moieties” could be various U-shaped systems, etc. (The

simpler MBBA and CNBP, Fig. 3, have also found application.)

Importantly, the above process would be enabled by the mutual proximity of the moieties within the crystalline lattice, an entropic facilitation that would largely overcome the steric barrier to the entanglements. Also, the entanglements would presumably facilitate the ensuing breakdown of the crystalline lattice upon continued heating.

Intriguingly, in fact, the entanglements would then become irreversible as the above proximity effect would be lost, so the entangled molecules would be forced to seek higher energy pathways for disentanglement. This indeed would eventually occur upon extended heating, with the breakdown of the liquid crystalline phase and the formation of the isotropic melt.

The above entanglements are also structurally plausible, as non-covalently bound stable molecular complexes are known in the form of catenanes and rotaxanes (Fig. 4) [15,16]. These interlocked molecules can serve as models for the molecular association in the liquid crystalline phase, which may be viewed as composed of quasi-catenanes and quasi-rotaxanes. These, of course, are metastable analogues that ultimately decompose once the isotropic melt is reached.

It is also highly likely that the above “loop-and-thread” process leads to the formation of nanoparticles of varying sizes, although a particular precursor would lead to a characteristic nanoparticle size [13,14]. The properties of the liquid crystalline phase, including its thermal range and stability, would be determined by the nature and size of these nanoparticles, as also their aggregation. This serves as an alternative to the current model based on molecular alignment (smectic, nematic, cholesteric, etc.). The aggregation of the nanoparticles does imply weak attractive forces, although not between molecules that are spatially aligned, as in the mesophase model.

Of particular importance is the fact that the stability of the liquid crystalline phase is a kinetic stability derived from the irreversibility of the molecular entanglements. Thus, unlike the mesophase model, the entanglement model does not rely on long range attractive forces that are unsustainable beyond the melting point of the crystal. In fact, the entanglements can only be

reversed upon cooling to recover the crystalline solid, although the entanglements can be randomly lost upon reaching the isotropic melt.

Thus, the entanglements lead to “sterically trapped” moieties—hence the catenanes and rotaxanes analogy—that possess a higher Gibbs energy barrier to disentanglement in the liquid crystalline phase than in the crystal lattice. (The relatively low Gibbs energy barrier to the interlocking that occurs in the crystal lattice initially, is thus noteworthy, being indeed key to the formation of the liquid crystalline state.)

In fact, the difference between a loose knot and a tight knot, as analogy for the entanglements in the crystal lattice and the liquid crystalline phase respectively, is rather apt. Thus, the liquid crystalline phase is characterized by entangled moieties that have strayed far from the original transition state for entanglement that occurred in the crystal lattice, hence cannot easily find their way back to the disentangled state. This explains the apparent paradox that the disentanglement is reversible in the crystal lattice but not in the liquid crystal at a higher temperature.

Thus, qualitatively, the transition state for disentanglement is narrowly defined in terms of conformational and steric features: the transition state is easier to reach from the crystalline lattice than from the liquid crystalline phase (essentially for proximity reasons as discussed above). The paradox of the thermal stability of the liquid crystalline phase is hence due to a phase change, as the highly ordered crystal lattice defines a very different molecular environment than the fluid liquid crystal. Thus, a comparison of the energies of the crystalline and liquid crystalline phases is complicated, indeed leading to the paradoxical thermal stability of an essentially metastable liquid crystalline phase.

The irreversibility of the entanglements in the liquid crystalline phase, therefore, is due to the change of phase, the entanglements having previously occurred in a different (crystalline) phase. Also, the stability of the liquid crystalline state over a temperature range indicates a relatively high specific heat, implying that the nanoparticle aggregate is undergoing changes without prejudice to the liquid crystalline state itself. These changes may well relate to aggregation, both in terms of the size of the nanoparticles and the average aggregation number.

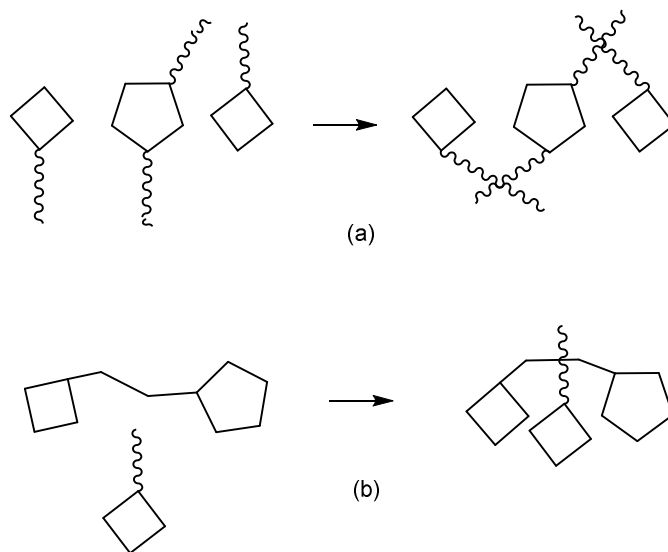


Fig. 2. Cartoon depiction of molecular entanglements in liquid crystals: (a) long chains (wavy lines); (b) U-shaped moieties

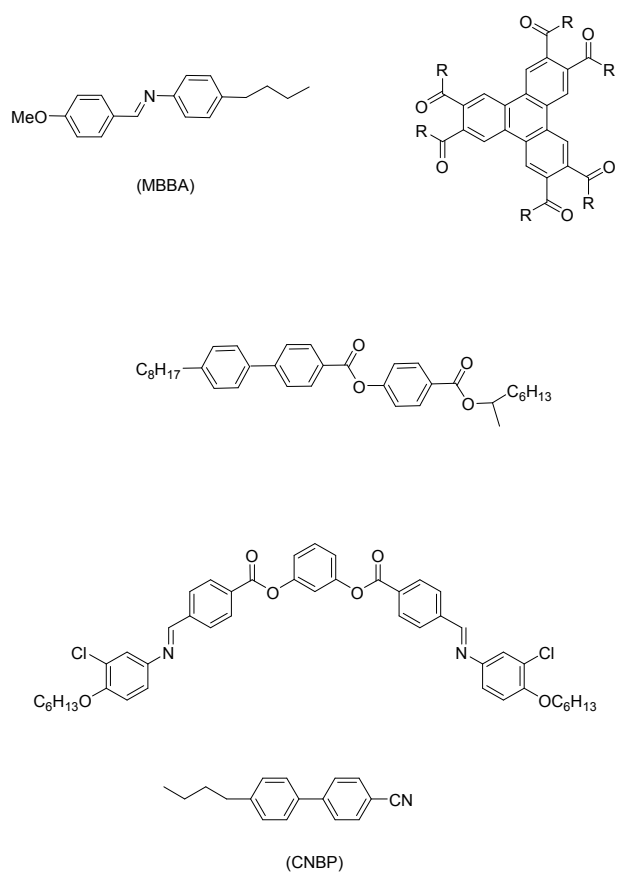


Fig. 3. Typical structures of compounds forming liquid crystals (adapted from ref. 5)

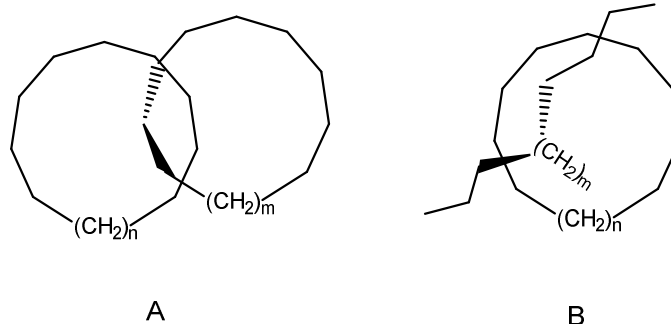


Fig. 4. Catenanes (A) and rotaxanes (B) in general

2.1.3 The problem of optical activity in liquid crystals: Enigma or opportunity?

As discussed briefly above (cf. 2.1.1) the formation of the liquid crystalline state is many a time accompanied by the development of optical activity [5,7,17-19]. Whilst this is unsurprising in the cholesteric cases (because of the chirality of natural cholesterol), it is indeed enigmatic in the case of achiral substrates (as discovered early on itself). Intriguingly, this phenomenon is the basis of the most important and widespread application of liquid crystals, i.e., in digital display devices. The enormous stability and reliability of these devices implies that the optical activity in liquid crystals has been evidenced beyond any shadow of doubt!

Early examples were apparently based on the “twisted nematic effect” (TNE), in which a twist was imparted to a nematic liquid crystal, thus leading to a discernible optical activity. This was explained as arising from the helical chirality of a nematically ordered set of molecules (produced by the imparted twist). However, there are two problems with the TNE: Firstly, the assumption of the nematic state, which is now invalidated in a general sense (*vide supra*); and secondly, the fact that optical activity requires molecular level chirality, which cannot be produced by mechanical twisting that only imparts chirality at the macroscopic level.

The discovery of the original TNE implies that optical activity is observed only upon mechanical twisting. However, it is possible that the twisting leads to an enhancement of a latent optical activity that is too weak to be observed per se. The latent optical activity must result from a molecular level chirality that could be subdued for several reasons. In particular, the translucent nature of the liquid crystalline phase implies poor

transmission of plane polarized light, which would reduce the sensitivity of the measurement of optical activity.

It is also possible that the molecular level chirality leads to the formation of a racemate with a relatively low barrier to chirality inversion. The twisting could then provide just sufficient helical chirality to the medium as a whole, to shift the equilibrium between the enantiomers in the racemate towards one form. This is plausible because of the unique liquid crystalline phase that is essentially a suspension of nanoparticles in close contact with each other. Thus, an external twist may well be transmitted to the constituent molecules, thereby inducing an enantiomeric excess and an observed optical activity.

Another intriguing possibility is that the formation of the liquid crystalline state is accompanied by symmetry breaking, i.e., the “spontaneous” generation of an enantiomeric excess from an achiral state [5,20,21]. However, although this has been a topic of intense speculation vis-à-vis the phenomenon of parity violation, clear-cut evidence has so far proved elusive. Essentially, parity violation is believed to arise from an inherent chirality in matter derived from the weak nuclear force, that is possibly manifested in molecular level chirality, indeed leading to a fundamental explanation for biomolecular chirality. However, the “parity violating energy difference (PVED)” between enantiomers is too weak to be observed by normal methods, its putative amplification to discernible levels also remaining in the realm of speculation so far.

Intriguingly, however, a remote possibility apparently exists for the autocatalytic amplification of PVED in polymeric and crystalline systems (although without

experimental support) [21]. All the same, this leaves open the possibility—however slim—that the optical activity observed in liquid crystals arises via PVED amplification in some manner, perhaps originating in the crystalline precursor. In fact, the thermodynamic basis of reaction dynamics in the crystalline state may differ significantly from the solution phase, thus affording pathways for PVED amplification during the melting stage. (Interestingly, melting point differences have been reported between enantiomers, although these remain controversial. [22])

2.1.4 Molecular level chirality in liquid crystals: Achiral versus racemic forms

The above discussion would be meaningful if the molecules comprising the liquid crystalline state possessed chirality. Intriguingly, however, the majority of cases apparently involve achiral molecules, although closer inspection reveals the possibility of chiral isomeric forms as well. Thus, many of the molecules possess non-planar U-shaped conformers that can exist in enantiomeric forms (analogous to biphenyls), but with a low barrier to interconversion. Also, although the chiral forms may well suffer various types of strain in the U-shaped moieties, they would possess a significant entropy of mixing (worth $R\ln 2$) that would contribute to the Gibbs energy of stabilization. Thus, it is indeed possible that a substantial proportion of molecules would exist in such chiral forms.

Such systems would also possess a low energy barrier to interconversion between the enantiomers, which can occur either directly between the enantiomeric U-shaped systems or via the extended planar forms. This then affords a pathway for a “spontaneous” disequilibrium of the enantiomers via the above discussed possibilities, i.e., mechanical twisting or PVED amplification. Several compounds that possess the above structural features and form liquid crystals are shown in Fig. 3, to substantiate these arguments.

The twisting effect would operate once the liquid crystal has formed, whereas the (putative) PVED amplification would likely be linked to the melting of the crystal (including the above entanglement processes). In fact, it is possible that this may directly lead to one enantiomeric form from an achiral precursor (or at least produce a discernible enantiomeric excess). This obviates the shifting of an existing equilibrium with an

equilibrium constant of practically 1, noting the vanishingly small PVED value. (This is apparently the only possible route in the solution state, hence practically unviable.)

These processes are apparently beyond current theoretical understanding, but a cartoon representation of a putative energy profile is shown in the Appendix. To reiterate, as the formation of liquid crystals inevitably represents a change of state, the principles of equilibrium thermodynamics may not apply, the initial crystalline state disappearing in the process. It is this essential irreversibility that complicates understanding of the liquid crystalline state (noting that its persistence does not represent stability). The irreversibility is manifest in the fact that the molecular entanglements that originate in the crystalline state are not reversed within the liquid crystalline regime.

The above arguments imply that liquid crystals may well represent the only known case of PVED amplification (long suspected to be the origin of molecular chirality). Alternatively, the TNE possibly represents a unique case of chiral mechanochemistry, as the mechanical effect presumably leads to discernible optical activity [23]. (The combination of the two effects cannot be ruled out either!) Thus, the formation of liquid crystals appears to have a stereochemical basis that needs to be pursued further.

2.1.5 Electro-optical effects in liquid crystals

The most important practical application of liquid crystals lies in the digital display devices that are a key part of modern electronic gadgets and instruments. The devices are based on a remarkable electro-optical phenomenon of liquid crystals, which essentially combines optical rotation with a change in light transmittance that occurs upon the application of an electrical voltage [5,7].

Thus, liquid crystals that show the TNE (e.g., CNBP, Fig. 3) are encased in a cellular compartment, with an arrangement for observing the rotation of plane polarized light, as also electrical connections for the input of voltage (Fig. 5). The optical rotation is observed via a set of “crossed polarizers” which essentially cancel out the rotation due to the liquid crystal, and a mirror that reflects the transmitted (polarized) light back to the observer. The transmittance is greatly reduced when a voltage is applied, so the

system nearly becomes opaque, although this is entirely reversed when the voltage is turned off. This is thus an ingenious optical device that is sensitive to an electrical voltage (corresponding to the signals emitted by the gadget).

Current explanations are based on the idea that the application of an electrical voltage also (essentially) racemizes the liquid crystal: this apparently stymies the crossed-polarizers arrangement, thus inducing opacity. However, in view of the ambiguities surrounding the TNE phenomenon (*vide supra*), this explanation for the electro-optical effect may need to be reassessed. In particular, it is highly dubious that the liquid crystalline sample employed can be reversibly racemized—indeed over a nearly infinite number of cycles—in the manner assumed: Clearly, the racemate cannot regain its original chirality without a chiral medium! (The cycles apparently involve repeated untwisting and twisting of the nematic phase, manifesting as the loss and recovery of the optical rotation.)

However, it is possible that the application of the electrical voltage changes only the transmittance of the light, without affecting the optical activity in any way (whatever its origin). This could be the result of changes in the size and aggregation of the constituent nanoparticles, as induced by the applied voltage. Further studies are apparently needed to clarify the above intriguing electro-optical phenomenon, for both theoretical and practical reasons. (The orientational order and anisotropic effects observed in the presence of an applied voltage, do not imply that they are a permanent feature.)

The above electro-optical effects represent a triumph of cooperative applied science, having evolved at the crossroads of exploratory

chemical science and electronic technology. The electro-optical effects are clearly among the most remarkable scientific discoveries of the twentieth century, their practical exploitation in the display devices being a stunning example of technological innovation involving necessity, coincidence and ingenuity.

2.2 Polymers and Macromolecules

2.2.1 Current views: Macromolecular aggregation and the “polythene enigma”

The phenomenal mechanical properties of polymers are bettered only by metals, with polymers often being less reactive and more stable (towards corrosion, etc.). These properties have led to the widespread use of polymers for a variety of applications, these ubiquitous materials par excellence thus serving almost as a defining characteristic of modern civilization [24].

A scientific understanding of the properties of polymers has been based on the obvious point of difference between polymers and normal (organic) compounds, i.e., the macromolecular constitution of polymers. Essentially, this has led to the view that non-covalent intermolecular forces—however weak—are amplified additively in macromolecules, which are thus aggregated enormously relative to simple molecules.

A problem—and a simple one at that—with this view is that the non-covalent intermolecular forces remain weak at the level of the sub-units of the macromolecules [6]. Thus, the clearly enormous intermolecular forces of attraction would be nullified by an equally enormous molecular size, in the case of macromolecules.

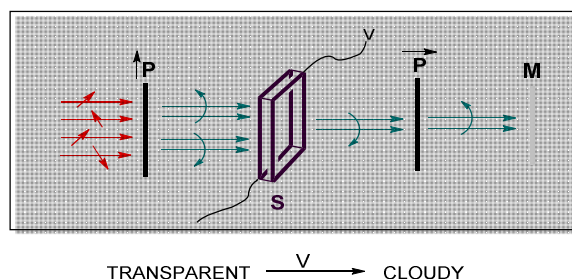


Fig. 5. A simplified depiction of the crossed-polarizers experiment: ‘P’ (vertical and horizontal polarizers, cf. orthogonal arrows), ‘S’ (liquid crystal sample) ‘V’ (voltage) ‘M’ (mirror); the randomly oriented incident light is plane polarized by the first ‘P’ (the resulting right and left circularly polarized light is shown by curved arrows); the rotation of this by ‘S’ and ‘P’ is represented by the presence of one type of circularly polarized light (reproduced from ref. 5)

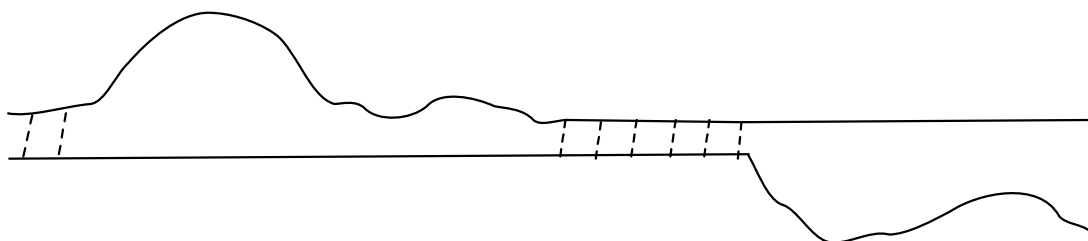


Fig. 6. Macromolecular aggregation with putatively weak van der Waals force (dashed lines)

A likely consequence of this fact is that the aggregation of macromolecules would appear wave-like, as the binding constant at each point would be small (Fig. 6). This would be particularly true in the case of polyethylene, which involves only weak dispersion forces (van der Waals, etc.), although high density polyethylene is possessed of great strength and hardness. It seems unlikely that this can be explained on the basis of poorly (“momentarily”) aggregated molecules!

In fact, a similar critique applies to most other polymers which are generally aggregated by weak dipolar forces. (Hydrogen-bonded aggregation, as in Bakelite, would be an exception, because of the relative strength of the hydrogen bond.) Clearly, therefore, the additivity of weak non-covalent forces does not provide a satisfactory explanation for the observed mechanical properties of polymers in general.

2.2.2 Driving forces for macromolecular aggregation: The critical role of entropy

A defining characteristic of polymers is the aggregation of its constituent macromolecules. There are apparently two principle driving forces for the aggregation of macromolecules, which may be termed competitive and non-competitive.

- (a) Competitive aggregation occurs in competition with solvation [25], which involves a large loss of solvent entropy, essentially arising from the large size of a macromolecule. Thus, the larger the macromolecule the greater the loss of solvent entropy, with a shifting preference for aggregation. However, aggregation is accompanied by the loss of entropy of the macromolecules per se, so the balance between the two types of entropy loss determines the strength of the aggregation. (Indeed, the remarkably low entropies of mixing attending polymer dissolution

strongly supports the possibility of a substantial loss of solvent entropy [6].)

- (b) Non-competitive aggregation is determined by the absolute loss of entropy of the aggregating macromolecules. In the absence of solvation, however, aggregation is the only way in which macromolecules can be stabilized. Thus, the loss of entropy accompanying this mode of aggregation is critical to determining the strength of the aggregation and the derived mechanical properties of the gross polymer.

A priori, of course, the fact that macromolecules are indeed aggregated implies that loss of entropy does not prohibit non-competitive aggregation! However, an analysis of this mode is not simple, the entropy effect being intriguingly subtle. In fact, it is important to choose the right standard of comparison for a proper understanding of the phenomenon.

2.2.3 Quantitative estimates of the weak forces: How “weak”?

The enigma of polymer strength and stability essentially derives from the perceived weakness of the non-covalent forces responsible for the aggregation of the constituent macromolecules. Thus, a clear understanding of the weak forces, particularly their quantitative estimation, is necessary to understand polymer properties and behavior. It is useful to focus on the quintessential van der Waals force, involved in the aggregation in polyethylene, for a general discussion of the problem.

The van der Waals force is believed to arise from the attraction of instantaneous dipoles, themselves created by the imperfect shielding of the nuclear charge by the electron cloud, in neighboring atoms [26,27]. (This apparently implies that the forces involve the nucleus of one

atom and the electron cloud of a neighboring atom.) Despite the (perhaps) speculative basis of the van der Waals force, however, they have been experimentally verified, particularly as evidenced in the formation of inclusion complexes. (The van der Waals force remains of key importance in supramolecular chemistry, including the related areas of enzymology and drug action.)

In fact, the existence of the van der Waals force had been theoretically presaged in the early work on the ideal gas law, a deviation from ideality presumably arising from weak attractive forces between the constituent molecules. Furthermore, although quantitative estimates derived from non-ideal behavior in gases pegged the strength of the van der Waals force at $\sim 1 \text{ kcal mol}^{-1}$, apparently, the enthalpy and entropy components were not considered.

Thus, the value was essentially estimated on the basis of an equilibrium constant for the weak association of the gas molecules, hence leading to an overall Gibbs energy estimate. (In fact, a Gibbs energy of interaction of $\sim 1 \text{ kcal mol}^{-1}$ implies an equilibrium constant of ~ 0.5 at normal temperatures, i.e., partial aggregation at best, in the case of macromolecules!)

However, an intriguing thermodynamic approach based on the van der Waals equation of state (Eq. 1) indicates that the van der Waals force may indeed be much stronger than currently estimated [6]. (In Eq. 1, n = no. of moles; R is the gas constant, T the absolute temperature and V the volume; a and b are the van der Waals coefficients.)

$$P = [nRT/(V - nb)] - a(n/V)^2 \quad (1)$$

Eq. 1 was originally conceived to explain the deviations observed from the ideal gas equation in real gases; in particular, coefficients a and b dealt with deviations in pressure and volume, respectively. The deviations were attributed to the formation of unstable complexes derived from weak intermolecular forces, that were not considered in the theory of ideal gases.

Furthermore, the coefficient a was identified with the equilibrium constant for the formation of the above van der Waals complex that causes the deviations (based on a consideration of the relevant units [6]). This leads to a low Gibbs energy of formation of the complex, based on typically observed values of a , apparently

justifying current estimates of the van der Waals force.

Interestingly, however, the formation of the complexes is accompanied by a large negative entropy change, which was neglected in the classical estimate of the van der Waals force. In fact, this may be estimated from available entropy data [26,28] as $\sim 50 \text{ e.u.}$ When this was included in the Gibbs energy of formation of the van der Waals complex it led to the standard enthalpy change, thus estimated $\sim 16 \text{ kcal mol}^{-1}$ [6].

This astonishingly large value, however, also implies that the van der Waals force is stymied by a large loss in entropy. A possible theoretical implication could be that the weak (non-covalent) interactions are dominated by entropic effects (because of the low enthalpy changes involved), whereas the strong (covalent and ionic) interactions are dominated by a relatively large enthalpy change. (These arguments concerning the relative entropy loss in the weak and strong interactions indicate an intriguing sigmoid relationship between the changes in enthalpy and entropy, cf. Appendix.)

In fact, an intriguing practical consequence would be that the van der Waals force can be manifested, in large measure, if the corresponding entropy loss is "damped" in some manner. Indeed, this may well be the thermodynamic basis for macromolecular aggregation!

2.2.4 Entropy changes determine macromolecular aggregation

Any complexation would be accompanied by a loss in entropy, but the case of macromolecular aggregation is interestingly complicated. In fact, it would be useful to compare the aggregation of macromolecules with that of the constituent monomer units.

Thus, the aggregation of m macromolecules each composed of l monomer units would be accompanied by the loss of entropy of m molecules; however, in the case of the aggregation of a corresponding number of monomer units, the loss in entropy would correspond to lm molecules. The difference in the entropy loss ($lm - m$) would, of course, be moderated if the vibrational entropy is included, as this would be significant in the case of the macromolecule [29].

All the same, at least qualitatively, the loss in entropy in the aggregation of macromolecules would be manifestly lower than in the case of a comparable set of monomers. (Importantly, the enthalpy component would be practically identical in the two cases.) And this implies that a large part of the enthalpy change in the van der Waals interaction would be manifest in the aggregation of macromolecules. This, apparently, is the likely driving force for the non-competitive aggregation of macromolecules.

Thus, the thermodynamic basis for macromolecular aggregation is intriguingly complex, and apparently depends on a subtle manifestation of a large part of the enthalpy of the van der Waals force (and other weak interactions, in general). However, the aggregation per se, and the material properties of the resulting polymers, would otherwise remain inexplicable and mysterious.

2.2.5 Thermodynamics of weak interactions: Basis and consequences

If the van der Waals force is inherently stronger than believed (in enthalpy terms) as argued above, it calls for renewed theoretical modeling of the force. Current models based on instantaneous dipoles may be inadequate in accounting for the above findings [26,27]. In fact, it is possible that partial overlap of electron clouds in the interacting atoms occurs in the van der Waals force: although this would involve filled orbitals, the resulting electron repulsions, however, would account for the weakness of the force (relative to covalent interactions).

A clear consequence of the above arguments and findings is that macromolecular aggregation, and the defining characteristics of polymers deriving from it, are now on a firmer footing, with the “polythene enigma” being less mysterious than before! Indeed, a Gibbs energy of $> 5 \text{ kcal mol}^{-1}$ for the weak non-covalent force in general, would mean practically total aggregation at all contact points at normal temperatures. Intriguingly, in fact, this is a theoretical requirement for the explication of the observed properties of polymers.

3. CONCLUSION

3.1 Liquid Crystals

Liquid crystals continue to play a pivotal role in modern electronic gadgetry and instrumentation, via the digital displays that serve as their critical

components. Despite their ubiquitous presence in the modern home and office, however, the theoretical basis of liquid crystals remains unclear. This is because the current mesophase theory of liquid crystals seems dubious, as the posited weak long-range intermolecular forces would be unviable above the melting point of the crystalline precursor. The observation of optical activity in some liquid crystals derived from achiral precursors is also mysterious: The electro-optical effect based on the twisted nematic effect (TNE)—key to the display devices—thus represents a defining enigma combining the theoretical and practical aspects of liquid crystals.

However, it seems likely that liquid crystals are formed via the entanglement of certain molecular moieties in the crystalline precursors, possibly in the incipient melt. These moieties are possibly long chains and U-shaped systems, their entanglements becoming irreversible once the liquid crystalline state is formed. The irreversibility essentially arises from a change of state and manifests as the persistence of the metastable liquid crystalline state over a relatively high temperature range.

Furthermore, the above entanglements likely lead to the formation of quasi-catenane and quasi-rotaxane systems that are decomposed only upon reaching the isotropic melt. Thus, the liquid crystalline phase apparently represents a suspension of nanoparticles, their size and aggregation defining the nature of the liquid crystal (currently viewed as smectic, nematic, etc.).

The optical activity in liquid crystals likely arises from chiral forms of the precursor molecules, in which U-shaped conformers can exist as rapidly interconverting atropisomers. The predominance of one chiral form in the equilibrium then represents a case of the “spontaneous” generation of optical activity, although two mechanisms may be envisaged. In one, based on the putative TNE, a mechanochemical action on the suspension possibly shifts the equilibrium between the chiral atropisomers towards one chiral form. Alternatively, an amplification of the parity violating energy difference (PVED) may be involved: Although elusive and controversial, PVED enhancements have been claimed to be feasible in polymers and crystals. All the same, the observation of optical activity in liquid crystals remains perplexing, straining current theoretical constructs and frameworks.

3.2 Polymers and Macromolecules

Although polymer properties manifestly derive from the aggregation of the constituent macromolecules, the thermodynamic basis of the aggregation phenomenon is complex. The essential problem is that the non-covalent intermolecular forces believed to mediate the aggregation are too minuscule to account for the observed binding. (This is particularly apparent in the case of the van der Waals forces that lead to the aggregation of polyethylene molecules.)

Current theory is based on the idea that the intermolecular forces are additively amplified along the polymer chain, but this flounders around the fact that the polymer molecule is correspondingly large, so the intermolecular forces remain minuscule at the level of the subunit. However, an analysis of the van der Waals force indicates that it is inherently stronger than believed in enthalpic terms, but is stymied by a large loss in entropy. This is apparently because, in general, the weak forces are dominated by entropy as the enthalpy change is small (relative to that in covalent and ionic binding).

A reassessment of the van der Waals force based on the original van der Waals equation of state, in fact, indicates a value ~ 16 kcal mol⁻¹ for the enthalpy change. However, an estimated large negative entropy change (~ 50 e.u.) nearly nullifies the enthalpy term, leading to the observed low value for the van der Waals force (apparently a Gibbs energy of ~ 1 kcal mol⁻¹).

Intriguingly, this implies that if the entropy loss accompanying the van der Waals interaction can be countered in some manner, the enthalpic component can be manifested to reveal a much stronger force than believed. Indeed, this is likely what happens in the case of macromolecular aggregation, as the entropy loss is damped by the subunits being linked together in a polymer chain. (This enormously reduces the translational entropy of the individual subunits relative to the free monomeric subunits, so there is less entropy to lose in the macromolecule case.)

These considerations apparently indicate an intriguing sigmoid relationship between the enthalpy and entropy changes accompanying atomic and molecular interactions in general. Furthermore, the possibly large enthalpy

component in the van der Waals interaction implies that the current model, based on the attraction of instantaneous dipoles in neighboring atoms, needs to be reassessed.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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APPENDIX

Liquid crystals: The TNE and possible symmetry breaking

As discussed, the twisted nematic effect (TNE) is an intriguing phenomenon that apparently has no viable explanation. The TNE was originally discovered by Mauguin [5,7], and represents one of the most amazing and brilliant discoveries in experimental science. In the TNE, essentially, a liquid crystal derived from an achiral molecule develops optical activity when the sample is mechanically twisted. (The TNE is also the basis for the digital display devices that represent the most important application of liquid crystals.)

Current explanations for the TNE are based on the supposition that a nematic liquid crystal is imparted a helical twist, hence developing an overall chirality. However, as argued above (sections 2.1.3 and 2.1.4), this is invalidated by the fact that the mesophase theory is itself dubious, as also by the fact that optical activity requires molecular level chirality. Alternative explanations would involve either a chiral mechanochemical effect or symmetry breaking via PVED enhancement.

The chiral mechanochemical effect is based on the possibility that the liquid crystal involved in the TNE is composed of chiral molecules present as a racemate. Mechanical twisting changes the equilibrium composition of the enantiomers, that are likely U-shaped atropisomers set in a viscous matrix of nanoparticles, and which can transmit the twisting stimulus to the chirality of the molecules themselves.

The other explanation for the TNE is based on the intriguing possibility that the parity violating energy difference (PVED) is somehow amplified during the formation of the liquid crystal. Although PVED effects remain in the realm of speculation, they cannot be entirely ruled out as autocatalytic PVED enhancement seems plausible in ordered systems such as crystals and polymers [21]. Therefore, the observation of (apparently) spontaneous symmetry breaking in liquid crystals in the case of the TNE, may well be a clue worth pursuing.

Amplification of the PVED in the solution state is normally impossible, essentially because of its vanishingly small magnitude ($\sim 10^{-15}$ kcal mol⁻¹) [21]. The solution state amplification process, however, implies that a mixture of enantiomers that is practically a racemate is deracemized. It is intriguing to consider an alternative mode in which an achiral precursor is offered a choice of preferentially transposing to one of an enantiomeric set of products under the influence of the PVED. The solution state process, of course, would again be ruled out as the enantiomeric transition states would differ in energy by the insignificant PVED value. However, in an ordered restricted environment, e.g., in a crystal lattice, it is conceivable that the solution state limitation can be overcome.

Thus, the breakdown of a crystal lattice could possibly be represented by the energy profile diagram in Fig. 7, wherein two enantiomeric pathways possess different slopes — rather than differing energy barriers as in conventional profiles. Although such a profile is admittedly hypothetical, it bears stating that the breakdown of a crystal lattice may not be subject to the solution state kinetic theory that is essentially based on the Boltzmann law. This implies that conventional transition state theory does not apply under such conditions, and the feasibility of a process would be governed by the requirement of lower energy throughout the process. (Essentially, this implies that is no transition state barrier to be overcome.)

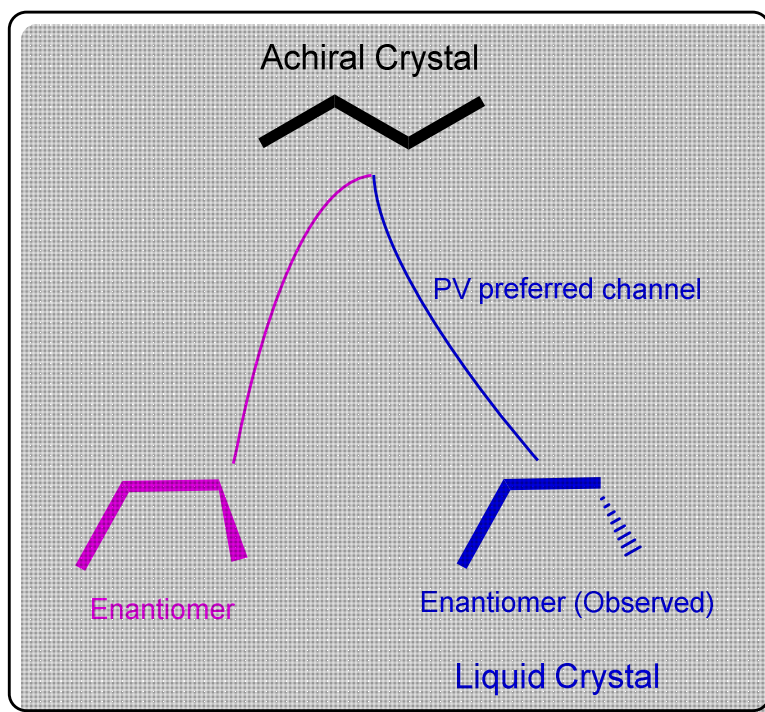


Fig. 7. Putative energy profiles representing the melting of an achiral molecular crystal under the influence of parity violation (PV) to form an optically-active liquid crystal

Furthermore, an autocatalytic process may well amplify a small but extant energy difference—such as the PVED—under such conditions. “Autocatalysis” here implies that the breakdown of the crystal lattice along a certain dimension is increasingly preferred as the collapse along that dimension occurs, relative to other modes and dimensions. These suppositions lead to the possibility that the preferred mode would possess a smaller slope than an alternative mode — possibly even a concave curvature, along which the transformation can slide (blue line in Fig. 7).

The formation of a liquid crystal upon the melting of an achiral crystalline lattice in the above manner, could thus lead to a discernable optical activity in the product. It is also possible that a small and barely measurable optical activity thus produced is amplified by the Mauguin twisting effect—combining the PVED amplification and chiral mechanochemical effects—leading to the observed TNE.

Polymers: An intriguing enthalpy-entropy relationship

The “polythene enigma” implies that the van der Waals force—as currently estimated—is far too weak to account for the observed strength of polymers. (The additive amplification of a weak dispersive force is nullified by a corresponding size of the macromolecule, so the interaction remains weak at the subunit level.) The van der Waals force, however, can be reassessed to indicate a remarkably strong interaction, essentially by separating its enthalpy and entropy components.

This leads to the view that the enthalpy of the van der Waals interaction can be as high as ~ 16 kcal mol⁻¹ that, intriguingly, pegs it way above the hydrogen bond (~ 5 kcal mol⁻¹). This, however, leads to the paradox that methane is a gas, whereas hydrogen-bonded water (of similar molecular weight) is a relatively high boiling liquid! A possible explanation for this conundrum would be that the entropy loss in the case of the van der Waals force is greater than in the case of hydrogen bonding, so the Gibbs energy values are inverted (relative to the enthalpies).

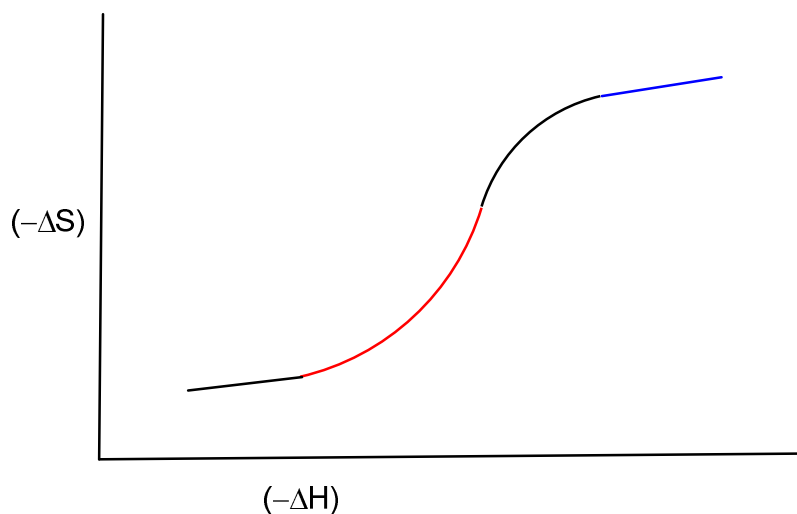


Fig. 8. Possible entropy (S) – enthalpy (H) relationships in intermolecular interactions

Although intriguing, this is indeed possible if the weak interactions (van der Waals, hydrogen bonding, etc.) are essentially dominated by the entropy effect. In other words, the entropy loss attending a weak interaction possibly increases exponentially with the enthalpy change, likely arising from a corresponding decrease in disorder. An increase in the bonding interaction clearly leads to enhanced proximity of the interacting species, with a corresponding loss in molecular freedoms.

Interestingly, a relatively weak long-range interaction would result in the loss of essentially translational entropy, closer contact resulting in the loss of vibrational and rotational entropy (in that order). This is because bond vibrations have a greater reach than molecular rotations, the latter thus manifesting sterically at closest contact (i.e., strongest interaction in terms of enthalpy). Furthermore, noting that vibrational entropy is lower than rotational entropy (based on the relative energy spacings), an exponential loss in entropy is indicated with increasing contact between the interacting molecules.

These arguments could explain the overall trends and the hypothetical enthalpy-entropy relationship depicted in Fig. 8. This sigmoid relationship essentially implies that practically all entropy has been lost by the onset of the strong bonding interactions (covalent and ionic, blue zone), which are further determined solely by the enthalpy change. The red zone represents weak interactions (van der Waals etc.), which experience an exponential loss of entropy with increasing exothermicity. Hydrogen bonding likely trails behind the van der Waals force (black zone), in an intriguing inversion of current views!

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