# A Scheme for Phase Stability in Liquid Crystal Polymers

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## SYNOPSIS

It is shown that conditions for realizing mesomorphic states in polymers are readily expressed in terms of the relative thermodynamic stabilities of the crystalline, liquid crystalline, and liquid phases. The simple scheme presented here has the merit of providing: (i) a unifying perspective over a wide range of mesophase behaviour that otherwise may be considered in isolation as disconnected occurrences, and (ii) a signpost for purposeful attainment (or enhancement) of the mesomorphic state also in the case of systems that are not normally considered liquid crystal forming. Examples are quoted from a range of materials, most comprehensively from polyethylene, bringing together diverse past and some rather striking new observations illustrating the validity and usefulness of the scheme.

## PURPOSE OF NOTE

In recent years, the mesomorphic state has come increasingly to the forefront of polymer science, particularly since the purposeful synthesis and study of polymeric liquid crystals. Most frequently, it is associated with the presence of mesogenic groups (such as on their own would form small molecular liquid crystals) built in, or attached to, the macromolecular chain where the mesomorphic state is usually attributed to the stiffness imparted by these groups. In other instances of mesophase forming stiff molecules, the chains are too irregular to crystallize, in which case the suppression of crystallization is considered the factor that promotes the mesophase. However, there are chains, including quite regular ones, that can give rise to the liquid crystalline state without any constituent capable of forming liquid crystals as separate small molecules. Such are, e.g., the polymers based on the flexibly jointed diphenyl compound diphenyl ethane,[1] the totally flexible main chain polysiloxanes with side groups beyond the length of methyl,[2] main chain polyphosphazenes,[3] and even the fully flexible and chemically

simplest long chain compound polyethylene under circumstances to be discussed in specific detail below. Many examples of mesophases in polymers of the latter type have been listed in the review by Wunderlich and Grebovicz.[4] The purpose of the present communication is to lay out a simple thermodynamic scheme that embraces all the above categories. It will be purely diagrammatic and qualitative, along familiar lines, yet we hope that in the context presented it will provide a coherent thread linking the various manifestations of mesophases, thus contributing to the understanding of their interrelation and providing guidance for their purposeful design. Illustrative examples will be quoted from available experimental material such as are not readily found all together in the literature, at least in the present context, and will embrace cases with chemical constitution and physical parameters as variables. They will include some examples of chains with varying ratios of rigid and flexible constituents, but mostly polyethylene in its diverse forms and circumstances.

## THE SCHEME

### Equilibrium States

For the considerations to follow it will suffice to consider the basic thermodynamic relationship

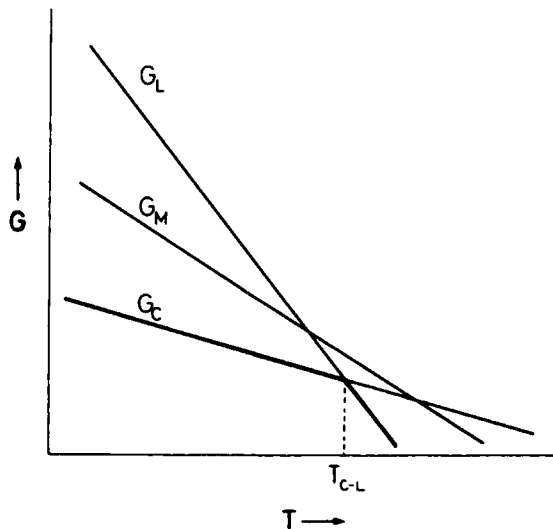---

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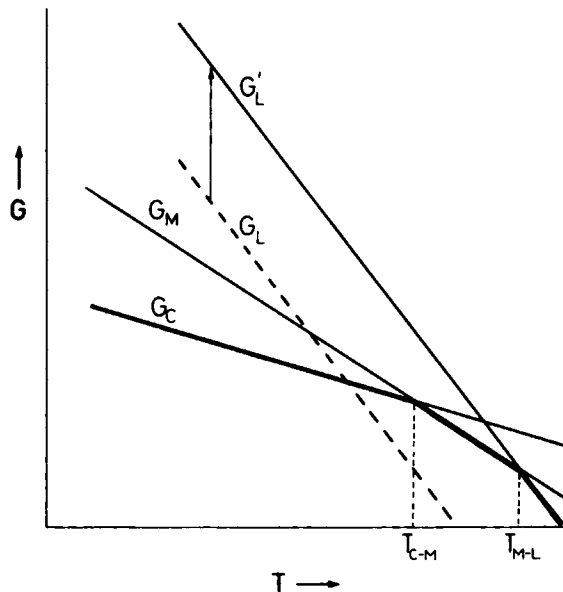
$$dG = V\,dp - S\,dT, \qquad (1)$$

where $G$ is the free enthalpy, $S$ the entropy, $V$ the volume, $p$ the pressure, and $T$ the temperature. For the scheme in question, take first the melting of a true crystal at constant pressure ($dp = 0$). As seen from Figure 1, and as follows from eq. (1), the free energies of both crystal ($G_C$) and isotropic liquid ($G_L$) decrease with increasing temperature where the decrease in $G_L$ is the steeper, due to $S_L > S_C$. Where $G_L$ crosses $G_C$, the crystal melts, which of course is at $T_{C-L} \equiv T_m$, the melting point of the crystal. In this case, as drawn in Figure 1, the free enthalpy of any hypothetical mesophase (if such can exist at all), $G_M$, cannot fall below both $G_C$ and $G_L$, and hence corresponds to a stable state at any temperature. While $G_M$ decreases faster with $T$ than $G_C$, it will only cross $G_C$ at a point above $G_L$, i.e., where the isotropic liquid is already the stablest phase. Thus, the mesophase is virtual and remains unrealizable as a stable phase.

To create a stable mesophase a section of the $G_M$ vs. $T$ curve will need to be brought beneath both $G_C$ and $G_L$ (thus to a state of greatest stability). This can be achieved either (a) by raising $G_L$ (Fig. 2) or (b) by raising $G_C$ (Fig. 3), or by a combination of both (a) and (b). As seen in Figures 2 and 3, the mesophase will be "uncovered" in a temperature
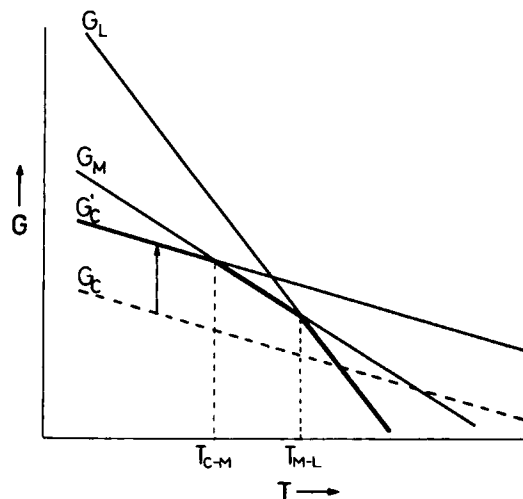


**Figure 2**  Schematic plot of free enthalpies vs. temperature for the system in Fig. 1 but with $G_L$ raised (to $G'_L$) so as to uncover the mesophase transition and the isotropization transition temperatures.

range bounded by $T_{C-M}$ and $T_{M-L} \equiv T_i$ corresponding to temperatures of crystal melting and isotropization, respectively. (The lowering of $G_M$ would have the same effect, but changes in $G_M$ are expected to be small compared to those in $G_L$ and $G_C$ and will be disregarded in what follows.) In general, raising $G_L$ (case a) arises from the lowering of the melt entropy, while raising $G_C$ (case b) from the reduction



**Figure 1**  Schematic plot of free enthalpies vs. temperature for a system that does not show a mesophase. $G_C$, $G_M$, and $G_L$ are, respectively, the free enthalpies of the crystalline, mesomorphic (virtual), and isotropic liquid states. $T_{C-L} \equiv T_m$ is the crystalline melting point. Here, as in subsequent Figs. 2–5, the heaviest lines correspond to the stablest state at a given temperature.



**Figure 3**  Schematic plot of free enthalpies vs. temperature for the system in Fig. 1 but with $G_C$ raised (to $G'_C$) so as to uncover the mesophase.

in the perfection of the crystal as to be shown in specific examples later.[†]

We can generalise further by considering the influence of change in pressure, i.e., the $V \, dp$ term in eq. (1). Usually, the specific volume is larger for the liquid than for the crystal with the mesophase expected to lie in between; hence, $(\delta G_C / \delta p)_T < (\delta G_M / \delta p)_T < (\delta G_L / \delta p)_T$. In principle, it could therefore happen that at some $p$ $G_M$ falls below $G_C$ and thus a mesophase may become "uncovered." It has been found that in most experimental systems (e.g., ref.[6]) the effect of increased hydrostatic pressure is to promote the mesophase ("barophyllic" behaviour).[‡]

The above scheme as it stands is for single-component systems leading to thermotropic mesophases. It can readily be extended, with appropriate elaborations, not to be pursued here, to two-component systems that would then also embrace the lyotropic state of matter.

## Metastable States

Figures 1–3 refer to states of thermodynamic equilibrium. However, systems may not respond immediately when passing from one stable regime to another within the phase diagram, hence, metastable phases can often arise.

In what follows we shall digress into the possibility of metastable states, as they are frequent in polymeric liquid crystals, and, in particular, as they generate an ambiguous nomenclature that we are anxious to clarify. The most commonly encountered metastability is that arising on crystallization. As familiar, crystallization only sets in at certain supercooling. In polymers in particular, crystallization temperature $T_{L \to C}$ can be appreciably below the equilibrium melting point $T_{C \to L} \equiv T_m$. On the other hand, the formation of a mesophase generally requires less supercooling. Now, if the temperature of the transition from the isotropic liquid to a normally unstable mesophase lies somewhere between $T_{C \to L}$ and $T_{L \to C}$, such a "virtual" mesophase may materialise on cooling. As the temperature is lowered still further, crystallization will occur. At this stage two extreme situations may be envisaged, as depicted in

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[†] Note that in case of (a) the crystal melting point, $T_m$, is raised, while in (b) it is lowered, a situation clearly brought out by the experimental examples to be quoted.

[‡] However, there is no fundamental reason that would make this a general rule. This is clearly illustrated by the example of the sequence of alkanes → polyethylene (see below, Fig. 8), where "barophobic" behaviour of short $n$-alkanes changes continuously with increasing chain length toward the "barophyllic" behaviour of polyethylene.[6]

Figures 4 and 5. On crystallization, the free enthalpy either drops from $G'_C$ to $G_C$, i.e., to the value for the perfect crystal (Fig. 4, where the broken line indicates a possible pathway), or there is no discontinuous change in $G$, i.e., a highly imperfect crystal is formed with its free enthalpy remaining at $G'_C$ (Fig. 5). The realistic path would be somewhere between these two extremes, i.e., some decrease in $G$ is expected that may not quite reach the level of $G_C$.

We shall first consider the extreme situations of Figures 4 and 5. When the perfect crystal of Figure 4 is reheated, it melts directly into the isotropic liquid at $T_{C \to L}$; thus, such a system displays the mesophase only on cooling, and is called "monotropic." On the other hand, the imperfect crystal of Figure 5 first changes back into the mesophase at $T_{C' \to M}$ and then into the isotropic liquid at $T_{M-L}$ on reheating; thus, the mesophase occurs both on cooling and heating and is called "enantiotropic." The latter case clearly illustrates that an enantiotropic mesophase does not necessarily mean stability of the mesophase, as sometimes implied, although a stable mesophase, naturally, must be enantiotropic. As mentioned before, real systems are between those described in Figures 4 and 5. Some decrease below $G_C$ will occur upon crystallization, the magnitude of the drop depending, among others, on crystallization kinetics. Accordingly, neglecting possible perfectioning on subsequent heating, mono- and enantiotropic behaviour are distinguished by the magnitude of the drop in $G$ on crystallization: If $G$ stays above a critical value ($G_C^c$) the system is enantiotropic; if
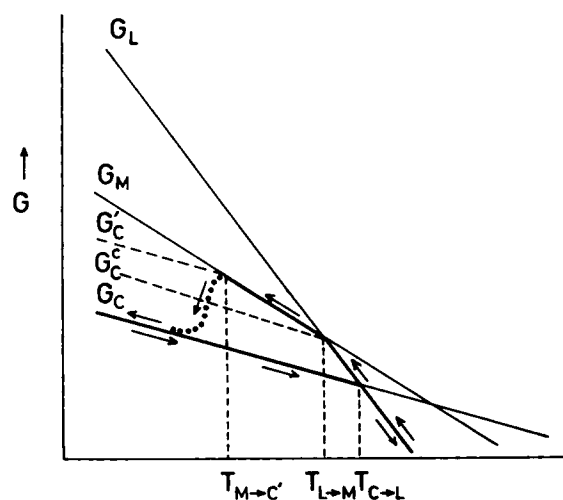


**Figure 4** Schematic free enthalpy diagram illustrating the origin of a monotropic liquid crystal (see text). Here, as in Fig. 5, the arrows represent cooling and heating pathways.
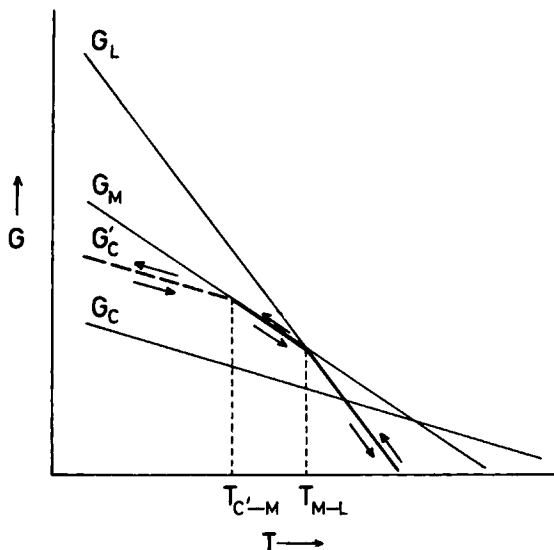
**Figure 5** Schematic free enthalpy diagram for an enantiotropic liquid crystal, where the mesophase is metastable (see text).

it falls below it is monotropic, the definition of $G_C^c$ being apparent from Figure 4. It is easily seen how crystal perfectioning on annealing can lead to a "conversion" of a monotropic into an enantiotropic mesophase, an effect frequently observed in both polymeric and small molecule liquid crystals.

While it was assumed above that only $G_C$ is affected by thermal history, in the case of main chain polymeric liquid crystals pronounced time dependent variability in $G_M$ has recently also been observed.[7] It was shown that the lack of equilibrium perfection in the nematic phase can lead to substantial depression of the isotropization temperature $T_{m-L} \equiv T_i$. Thus, nonequilibrium *mesomorphic* states can also, in principle, affect the phase sequence (enantiotropic, monotropic) in the case of polymeric liquid crystals.

It is worth noting further that, under certain conditions, polymers will also display superheating effects, in which case the mesophase may only appear on heating; this can be regarded as "monotropic" behaviour in the reversed sense. An example of this in connection with polyethylene will be quoted further below.

As seen from the above, kinetics will always play part in any LCP phase diagram as determinable in practice. Its influence on our present conditions will depend on its magnitude. If it is small enough, so as not to alter the sequence of appearance (or disappearance) of the different phases with changing temperature, the equilibrium situations in Figures 1–3 will be taken to apply with the kinetics as an

overlay, affecting only the exact numerical values of the actual divides. If, however, the phase sequence itself is affected, and in fact new phases are created due to metastability, then the whole phase behaviour will become kinetically determined and considerations in Figures 4 and 5 will pertain.

Finally, a further kinetic factor, the glass transition $(T_g)$, needs invoking, particularly pertinent to LCP-s. On cooling, the system becomes immobilised at $T_g$ (more precisely also dependent on the rate of cooling); hence, phase transformations will be arrested or altogether prevented. The inverse will apply when a previously immobilised system is heated above $T_g$ and the system will again be able to follow its course towards the equilibrium state. In practice, this will lead to inaccessibility of certain portions of the phase diagram or, conversely, lead to the freezing of the liquid or of the liquid crystal state enabling their attainments at temperatures where by thermodynamic criteria they would be unobtainable otherwise (isotropic or LC glass, respectively[4]). Even if $T_g$ is not a thermodynamic quantity, the indication of its location in the phase diagram can therefore serve a useful purpose.

Having placed metastability, glass transition, and related kinetic issues on the map, we shall resume our argument as referring to thermodynamic equilibrium alone.

## EXAMPLES—GENERAL

### Mesogenic Polymers

The scheme embodied in Figures 1–3 encompasses most known situations. Thus, high (or raised) $G_L$ (Fig. 2) corresponds to low melt entropy, which is consistent with the familiar tendency of stiff chains (wormlike or rigid rods) to give rise to mesophases. From this in turn follows the mesophase promoting role of mesogenic groups, the most often quoted single factor responsible for polymeric liquid crystals (LCP) and principal subject area of present-day LCP research. In fact, the whole presently active area of chemical stiffening of chains, so as to give rise to liquid crystals, all relies in the first instance on appropriate shifting of $G_L$ in the context of Figure 2.

The extreme limit of stiffness is the fully rigid rod, such as results from the polymerisation of all phenyl or other condensed ring-containing monomers of which poly(phenylene benzbisthiazole) (PBZT) of currently increasing topicality is a salient example.[7] In such cases of fully rigid rods, $G_L$ (or

even $G_M$) becomes so high that $T_i$ (or even $T_m$) may lie beyond the chemical stability limit of the molecule; in other words, the material becomes infusable (and also practically insoluble). As well known, this fact has given rise to the widespread activity of chemically loosening the liquid crystal forming rigid rods so as to make them more readily fuseable and soluble (i.e., processable) without, however, losing the mesophase "window" in the phase diagram.[†]

In present practice, the loosening of rigid rod polymers is being pursued by copolymerising rigid phenyl-containing mesogenic groups with flexible alkane or ethylene oxide spacers in varying predesigned ratios (e.g., refs.[10,11]). Here, the number of $CH_2$ (or $CH_2CH_2O$) groups within the spacer in the different preparations determines the overall flexibility/rigidity, longer spacers leading to more flexible molecules and vice versa. The corresponding $T_i$ will be higher with shorter spacers (e.g., ref.[8,9]) due to decreasing entropy of the isotropic liquid.

The above type of molecular tailoring of mesophases may well appear self-evident from the chemical point of view. Even so, its incorporation in an underlying thermodynamic scheme should be helpful for a purposeful planning of chemical design and perceiving wider interconnections. For this purpose, phase diagrams with chemical (e.g., spacer) composition as variable should be particularly appropriate, especially when the limiting conditions for the existence of mesophases are approached. Explicit reference to such phase diagrams will be made in the next section (and beyond in ref.[16]), in that case in connection with the influencing of crystal perfection with which this issue becomes combined.

Returning to Figures 1–3, the position of $G_L$, hence the existence or creation of mesophases, can also be influenced by physical means. Thus, orienting chains, which would otherwise be randomly arranged in the isotropic phase, and also stretching them (in the case of chain flexibility), will reduce the configurational entropy, and hence raise $G_L$, with consequent facilitation of liquid crystal formation. This LC-promoting effect of orientation is familiar among rigid or partially stiff liquid crystal polymers, as manifest, e.g., by the drop of viscosity when passing through orifices, a situation arising on processing (see e.g., ref.[12] on Kevlar). It is perhaps less familiar that fully flexible chains, which on their own are not liquid crystal forming (i.e., correspond to Fig.

1), can be transformed into a mesophase by orientation and constraints according to the scheme in Figure 2 to be invoked explicitly for polyethylene below.
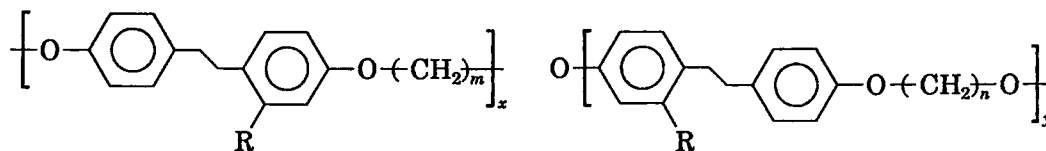
## Crystal Imperfections

High (or raised) $G_C$ (Fig. 3) indicates crystals that are either imperfect due to defects or, while otherwise regular, contain loosely packed molecules. The latter, i.e., loose packing, may be due to bulky side groups. The liquid crystal forming ability of the otherwise regular and fully flexible long side group containing siloxanes[2] could be relatable to this cause. In addition (or alternately), bulky side groups could, due to steric congestion, stiffen a chain that then will raise $G_L$, contributing to (or causing) LCP formation. The possibility of chemical irregularities, of course, are manifold in polymers. Irregularly placed branches or side groups, whether deliberate or accidental, are common features, again to be more explicitly referred to in connection with polyethylene. The LC-forming tendency will be particularly pronounced when the relatively bulky side groups and irregularity combine, as in the case of hydroxypropyl cellulose (e.g., ref.[13]). Here, the inherent stiffness of the chain is biassing the system in the same direction in any case by raising $G_L$, while the presence and irregular disposition of the sidegroups suppresses crystallization by raising $G_C$.

Introduction of comonomer units, even without necessarily involving branches, will similarly reduce crystal perfection, and hence raise $G_C$, thus promoting formation of the mesophase. Again, this will combine with the mesophase-promoting tendency of stiff units within the chain, when such are present in any case, as, e.g., in the technologically topical copolymers of hydroxybenzoic and naphthoic acids.[14]

Mesogen-flexible spacer systems are particularly amenable for controlled adjustments in phase behaviour through variation in copolymer constitution. As stated previously, introduction of flexible spacers can render otherwise rigid rod polymers fuseable. If, say, two different flexible spacer lengths are used, the resulting copolymers will have enhanced mesomorphic tendencies through raising of $G_C$, thus lowering $T_m$, the result being a widened $T_i - T_m$ interval in the phase diagram. Varying the copolymer composition ratio for, say, a given pair of flexible spacers then provides a subtle control over $T_i - T_m$, hence the width of the mesomorphic zone. This situation can be readily realized and systematically explored with polyethers of alternating diphenyl type

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[†] For processing purposes, fluidity alone is required. This is achieved once $T_m$ is reached. Hence, in practice the attainment of $T_i$ for the technologically important rigid rod type molecules (e.g., Kevlar, PBZT, Vectra—see below) is not usually pursued.

mesogens and alkyl spacers linked by ether oxygen. These compounds, synthetized and explored by Percec and collaborators,[1,15,16] possess sufficient thermal stability to permit the traversing of the var-

ious phase transitions without the danger of chemical changes, such as beset the more familiar, but otherwise analogous, family of polyesters.

Of these studies, here we shall illustrate one case involving chains with formulae such as



This is a copolymer where the "mesogen" itself is a semi-flexible moiety of diphenyl ethane, which is not LCP forming as a homopolymer, with $(CH_2)_{10}$ as a sole spacer, but is turned into LCP on copolymerization with $(CH_2)_8$ as the alkyl portion of the comonomer unit. The result is shown in Figure 6. We see that a stable mesophase ($T_i > T_m$) results beyond a $(CH_2)_8$ composition of 0.2, with $T_i - T_m$ being largest at around 1 : 1 $(CH_2)_8/(CH_2)_{10}$ ratio.

Choosing the more rigid $\alpha$-methyl stilbene, which is a familiar mesogen, instead of diphenyl ethane in the above family of polyethers enhances the LCP-forming tendency throughout. Here, $T_i$ lies always above $T_m$; hence, the mesophase is the stable one over the full comonomer composition range, again with $T_i - T_m$ being maximum at around the 1 : 1 ratio.[16]

The cases quoted thus provide examples for passing into the mesophase and for the controlled widening of this mesophase through chemical tailoring
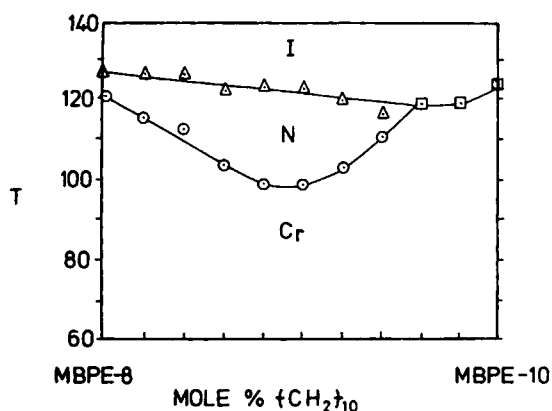


Figure 6  Crystal-isotropic (Cr-I), crystal-nematic (Cr-N), and nematic-isotropic (N-I) transition temperatures as a function of mole fraction of $-(CH_2)_{10}-$ spacer pertaining to the series of MBPE-8, 10 copolyethers, containing methylbiphenyl ethane mesogen and randomly distributed $-(CH_2)_8-$ and $-(CH_2)_{10}-$ spacers (adapted from ref.[15]).

in a systematic manner in accordance with basic thermodynamic principles.

Among imperfections we may count further the random placement of isomeric variants of otherwise identical chemical moities along the chain. The mesogenic character, of $\alpha$-methyl stilbene, a common mesogen,[10,11] is in fact partly due to this reason. Here, the presence of the methyl group introduces nonplanarity into the otherwise planar stilbene moiety.[17] Thus, two enantiomers are possible, the polymer itself having no stereoregularity. The result is that $G_C$ is raised and the melting point is suppressed; hence, 4,4'-substituted $\alpha$-methyl stilbenes, but not stilbenes, are nematogenic even as small molecules. When incorporated in a chain a further type of isomerism, namely head to head or head to tail (with relation to the methyl group in the mesogen), is added, the random sequence of which undoubtedly reinforces the LC-forming tendency through raising the imperfection content of the crystal. All the above, relating to the methyl stilbene polymer, relies on the raising of $G_C$ as in Figure 3. This clearly combines with the chain-stiffening effect of the stilbene group raising $G_L$ by Figure 2, the subject of the preceding section. The above case therefore provides an example of the mutually reinforcing interplay of the two thermodynamic factors highlighted by Figures 2 and 3, respectively.

The above merely serves to place chemical tailoring on the map within the broader framework of our scheme. This line, with the added variable of molecular weight, will be pursued further in a forthcoming publication specifically devoted to it.[18]

## EXAMPLE—POLYETHYLENE

### Crystal Imperfections

In what follows we shall proceed with examples on polyethylene that illustrate the main aspects of the

present scheme and at the same time are noteworthy in their own right.

Polyethylene conforms to the situation of Figure 1, i.e., under normal conditions it does not display a mesophase, only the familiar orthorhombic crystal form ($o$). Nevertheless, there exists a virtual mesophase that can be "uncovered"; the ways in which this can be achieved are the subject of what follows.

First we discuss the mesophase itself. This corresponds to a hexagonal packing of the straightened polyethylene chain, i.e., to the packing of rods of circular cross-section, that in turn arises through cylindrical averaging of the polyethylene chain around its axis. This virtual hexagonal phase ($h$) in polyethylene is in direct continuity with the stable hexagonal crystal phase in $n$-alkanes, as laid out by one of us elsewhere.[6]

Of the various ways of uncovering this virtual mesophase, we consider first the route by Figure 3, i.e., raising $G_C$. One example is provided by ethylene–propylene copolymers.[19] Here, for high enough copolymer content (for ca 70 $CH_3$ branches per 1000 main chain carbon atoms), the X-ray patterns reveal the hexagonal ($h$) as opposed to the familiar orthorhombic ($o$) packing of chains even at room temperature. Here, the randomly distributed ($CH_3$) branches disturb the regular packing of the chains, thus leading to the situation shown in Figure 3.

Another example is the influence of irradiation on linear PE with $\gamma$-rays or electrons[19] with doses large enough (more than 300 Mrads) to start influencing the $a$ spacing of the orthorhombic lattice, but not yet sufficient to appreciably reduce, or even less destroy, crystallinity (the latter happens well beyond 1000 Mrads). When such an irradiated sample is heated, the $o$ phase changes first into an $h$ phase before melting (Fig. 7). Thus, the irradiation has created a mesomorphic region in accordance with Figure 3, the temperature interval $T_i - T_m$ increasing with irradiation dose received (Fig. 7). As familiar by now, irradiation crosslinks the polyethylene chains, preferentially in the amorphous regions,[21,22] yet as the dose becomes large (approaching and exceeding 1000 Mrad) crosslinks are being increasingly created also in the crystal. The latter will produce lattice defects that will increase $G_C$ and thus, by Figure 3, will lead to a stable mesophase in the appropriate temperature region with lowered $T_m$. It is worth noting that the introduction of crosslinks also affects $G_L$: By reducing the configurational entropy of the melt it will raise $G_L$, and hence lead toward the situation shown in Figure 2. (There is evidence for it through an initial *increase*—as opposed to the subsequent overall decrease—in the $o$ melting point

at doses that are too low, 5–20 Mrad, to have other consequences for the phase diagram.[19,20] Thus, we have a situation where an increase in both $G_C$ and $G_L$ (Figs. 3 and 2, respectively) contribute to the uncovering of the mesophase.

As laid out earlier, hydrostatic pressure could promote the mesophase. Polyethylene provides a good example. As explored by Bassett et al.,[5] a hexagonal phase with mesophase characteristics (no longitudinal register between chains, high chain mobility enabling ready sliding of chains) appears above 3 kbar pressure—even with the (chemical) defect-free linear PE, at a suitably elevated temperature (Fig. 8). Now, if the chain contains chemical defects, such as crosslinks produced by irradiation, the triple point will shift toward lower pressures with increasing crosslink content until the hexagonal phase will become stable, even at atmospheric pressure.[20] The latter is, in fact, the situation in the preceding paragraph represented by Figure 7, thus highlighting the continuity between the effects of crosslinking and pressure: Both increase $G_L$ by reducing the entropy of the liquid, with the crosslinks also increasing $G_C$.[†]

Figure 8 also displays the connection between the stable hexagonal phase in short $n$-alkanes and the hexagonal mesophase in polyethylene as a function of chain length in the $p - T$ diagram. A full discussion is given by one of us elsewhere.[6] At this point our emphasis is on the continuity, despite the fact that the pressure coefficient of the width of the temperature interval is of opposite sign in these two families of material. This continuity is apparent also by a structural feature, namely the concentration of conformational "kink" defects, $C_K$. As described in ref.[6], $C_K$ can be directly registered spectroscopically and inferred from X-ray diffraction, and is found to be a continuous function of temperature ($T$) and chain length $l$. The mesophase ("rotator" and "hexagonal" phase) appears in different systems under different conditions, and the corresponding $C_K$ ($l$, $T$) values lie on a master surface given by an appropriate set of $l$, $T$ coordinates. The gradual changeover from "barophobic" to "barophillic" behaviour of the mesophase with increasing $l$ and $T$ is attributed to the steeply increasing configurational

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[†] Dependent on whether the rise in $G_L$ or that in $G_C$ is dominant, the crystal melting point will be higher or lower than for the corresponding linear material under atmospheric pressure. This follows from Figures 1–3 (see footnote [†] there) and is clearly reflected by Figures 7 and 8 where $T_m$ values (here the $o \rightarrow h$ transition) can be both elevated (Fig. 8 and high-pressure entries in Fig. 7) and lowered (1-bar entry in Fig. 7).
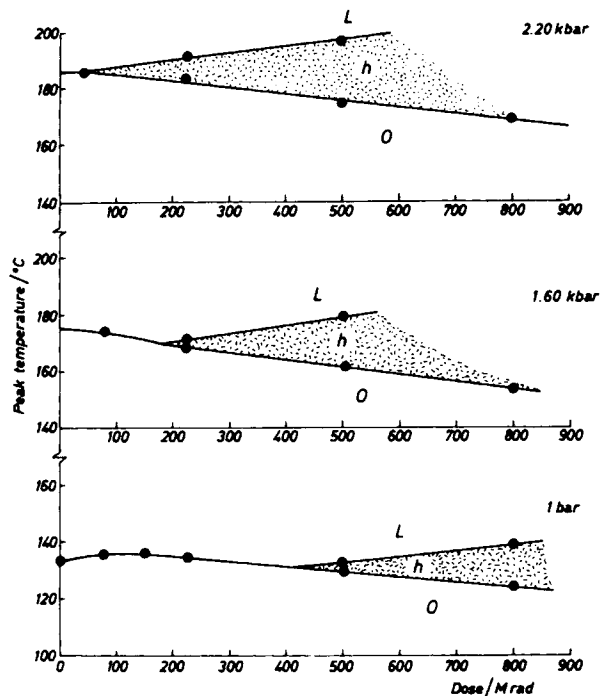
**Figure 7** Transition temperatures $T_{C-M}$, $T_{M-L}$, and $T_{C-L}$ at three pressures of irradiated polyethylene as a function of radiation dose. Here the mesophase is the hexagonal phase ($h$, shaded), the crystal the orthorhombic phase ($o$), and the liquid ($L$) is the melt (Vaughan et al.[20]).

entropy associated with the introduction of "kinks," while maintaining a comparatively low volume.[6]

## Orientation

While still with PE, we pass on to situations conforming to Figure 2, i.e., to the uncovering of the mesophase through raising of $G_L$. For a flexible chain like PE, the latter is realized by stretching out of the chains and keeping them stretched,[23] or otherwise constrained,[24] while in the melt (or solution), thus preventing the full conformational entropy to be recovered. Since in ultraoriented (and thus ultrastrong and stiff) PE fibres the molecules are virtually fully stretched out, they lend themselves well to the creation of such a situation. Such fibres, when held at fixed length, are heatable beyond their usual orthorhombic crystal melting point, when within an appreciable temperature interval and, for a limited time, the hexagonal form is apparent. Here the DSC scans display two melting peaks corresponding to $o \rightarrow h$ and $h \rightarrow L$ transformation as verifiable by X-ray diffraction.[25,26] In such a situation (realized by holding fibres clamped at their ends,[23,25] or constrained through embedding in a resin[24,26]), the mesophase is necessarily transient as the chain ori-

entation will relax in time; such a situation therefore will not correspond to a final equilibrium.

An equilibrium situation, however, can be approached by *light* crosslinking of the fibres, where the crosslinks are too few in number to significantly influence the thermodynamic stability of the solid phase (say, to 10 Mrad dose as compared to several hundred Mrad quoted in Fig. 7), but nevertheless are sufficient in number to create a loosely connected infinite network. Such a network can be stretched out into a highly oriented system, either in the melt as an elastomer, or in the partially crystalline state through usual fibre drawing. There are several reports, past[27,28] and more recently relating to high-modulus fibres,[29,30,31] of such lightly crosslinked oriented systems converting to, or forming in, the hexagonal phase above the crystallization or melting temperature of the usual orthorhombic crystal form. Here, when held at constant length the stress, and with it the hexagonal form, can be maintained over a considerable length of time, if not indefinitely, and
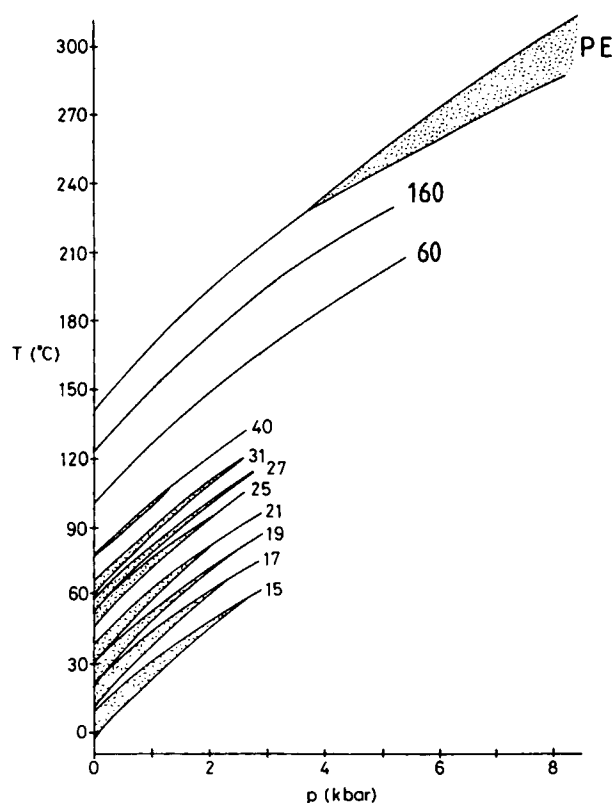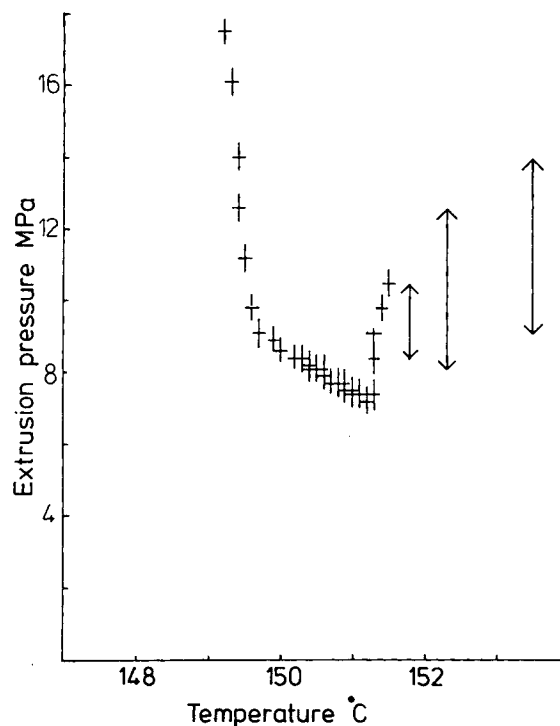


**Figure 8** Pressure–temperature diagrams of $n$-alkanes and polyethylene. Shaded areas indicate regions of stability of the mesophase (hexagonal or rotator) with the liquid (melt) phase above and the stablest orthorhombic crystal phase below. The figures indicate the number of carbon atoms in the chain (from Ungar[6]).

can also be reconstituted after repeated cooling and heating into the orthorhombic and liquid regimes. This suggests that genuine equilibrium according to Fig. 2 may be attainable, inviting renewed explicit investigations to this effect.

Finally, we quote a most recent finding that seems to fall into the above scheme and is of potential practical consequence.[32-34] Very high-molecular-weight (MW) PE melts behave in a highly elastic manner: They do not stretch (or flow) or extrude smoothly, but fracture and spurt respectively instead. The latest work here, however, identified a narrowly and sharply defined temperature window (under existing experimental conditions between 150-152°C) where such material extrudes smoothly with surprisingly low flow resistance ("viscosity"). Below 150°C, the viscosity rises sharply until on further lowering of temperature the system blocks, while above 152°C it extrudes in spurts at increased mean extrusion pressure. Figure 9 shows a pressure vs. temperature curve at a constant exit velocity (piston speed in rheometer) for a polymer of $M_w$ = 410000, displaying the sharp minimum between
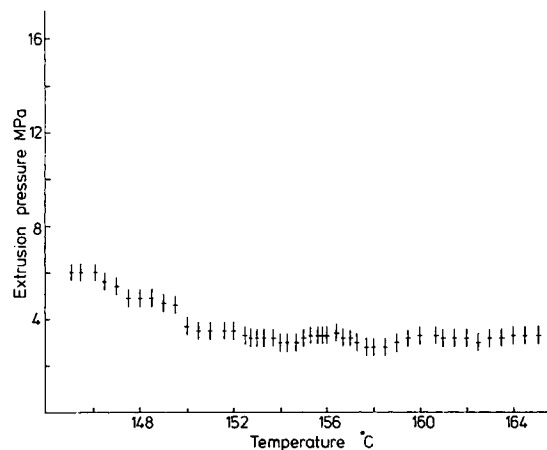


**Figure 10** Extrusion pressure plotted against extrusion temperature for extrusion of a polyethylene of $M_w$ = 2.2 × $10^{-5}$ during heating at approximately 0.2-0.6°C min$^{-1}$. Approximate piston velocity 3.3 × $10^{-2}$ cm min$^{-1}$. 1 mm diameter die. (From Waddon and Keller.[32])

150-152°C. This is to be compared with the "normal" extrusion behaviour displayed by a polymer with $M_w$ = 220,000 (Fig. 10), i.e., no minimum in pressure, only a steady decrease with temperature, under otherwise identical conditions.

To our mind, the existence of the above temperature window must be associated with the presence of a distinct new phase that has all the hallmarks of a liquid crystal mesophase, hence for polyethylene the hexagonal phase. Accordingly, it is tempting to assume that the lower temperature end of the window would correspond to an $o \rightarrow h$ transformation, while the upper end (sharply defined within 0.2°C) to $h \rightarrow L$ transformation. The ensuing spurt corresponds to the usual behaviour of such high-molecular-weight melts at conventional processing temperatures, where such materials are in practical terms unprocessable. In the above situation, the reason for mesophase formation would lie in the transient alignment of the chains while passing through the conical portion (with decreasing cross-section) of the extrusion barrel on their way to the die exit. Here the flow field will be elongational, which is known to be the requirement for stretching out chains (e.g., ref.[35]). It is known from work on solutions, and from preceding theoretical predictions (see, e.g., ref.[35]), that such elongational flow-induced chain stretching is critical both in strain rate $\dot{\epsilon}$, with a critical value $\dot{\epsilon}_c$, the coil → stretch transition, and in molecular weight (MW), $\dot{\epsilon}_c$ being a sharply decreasing function of MW. The critical dependence of the effect on MW for a given $\dot{\epsilon}$ (defined by the polymer exit—hence piston velocity in the rheome-



**Figure 9** Extrusion pressure plotted against extrusion temperature for extrusion of a polyethylene of $M_w$ = 4 × $10^5$ during heating at approximately 0.3-0.4°C min$^{-1}$. Approximate piston velocity 5 × $10^2$ cm min$^{-1}$. 1 mm diameter die. The vertical, doubled headed arrow(s) represent pressure oscillations in the region of spurt. (From Waddon and Keller.[32])

ter) is apparent from the comparison of Figures 10 and 9. There is a similar effect, i.e., the appearance of a pressure minimum in the pressure–temperature curves recorded at constant piston velocity, when surpassing certain piston speeds (hence $\dot{\varepsilon}$) demonstrating the existence of a critical $\dot{\varepsilon}$ for a given grade of polyethylene.[33,34] Clearly, the situation exemplified by Figure 9 falls within the scheme in Figure 2 with the added factor that the chain orientation, and consequent mesophase formation, is transient: it is confined to the duration of the appropriate passage time, and even then pertains only to the appropriate portion of the flow field. The flow-enhancing effect of the mesophase with respect to the melt is attributed to self-straightening and disentangling of polymer chains promoted by the $L \rightarrow h$ phase transition. Thus, the number of chain entanglements, which is so high in an ultrahigh molecular weight polymer as to prohibit flow of the melt, is appropriately reduced in the mesophase. On the other hand, the translatory chain diffusion remains high compared to that in the ordered orthorhombic crystals, accounting for the low flow resistance.

Admittedly, the existence of the postulated transient mesophase would still require structural confirmation. Even so, the taking of a sharp drop in viscosity as indicator of mesophase formation has well-established precedents in the liquid crystal field. Such is, e.g., the well-documented effect in Kevlar referred to above[12] that in many respects has similarities to the presently discussed PE, except that Kevlar is "mesogenic" and can exist as stable liquid crystal under ambient conditions, while the mesophase in the flexible PE is "virtual." The latter virtual phase only becomes real transiently, which suffices to dramatically affect the entire flow behaviour of the material, the effect through which it is being detected.

## CONCLUSION

It has been shown how the diverse manifestations of the mesomorphic state in polymers can be encompassed by a simple unifying scheme on the basis of elementary considerations of the relative thermodynamic stability, including metastability, of the crystalline, liquid crystalline, and liquid phases. The scheme embraces not only traditional LCPs with mesogenic groups but also flexible polymers such as may not be considered liquid crystal forming a priori, but nevertheless can be obtained as such by uncovering virtual mesophase regimes within their phase diagrams. As shown, the latter can arise in suitable chemical variants within a given family of compounds, and can be purposefully accomplished by

subsequently induced chemical modifications and also by appropriate choice of physical parameters and constraints, sometimes with quite unsuspected results (e.g., the transient mesophase and consequent narrow processing temperature window in high MW polyethylene). Since few other polymers have been studied as comprehensively as polyethylene—the polymer of most of our examples—it may well be that many more polymers not considered mesogenic at present will be found to exhibit mesomorphic behaviour under appropriate conditions. The present note, among others, should hopefully provide signposts for the purposeful creation of mesophases and for their uncovering—in cases where they may be hidden—on the basis of simple thermodynamic considerations.

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