HIERARCHICAL STRUCTURE IN POLYMERIC SOLIDS AND ITS INFLUENCE ON PROPERTIES

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INTRODUCTION

As proposed originally this is a multifaceted project centred on liquid crystal forming materials (LC) encompassing the hierarchical structures arising therefrom and the influence of flow and orientation on their formation. During the past 5 months this subject became established in our laboratory, the chief emphasis being on the choice of suitable model materials to serve as a basis for all future work. In this respect we were very fortunate and, given the fact that we only just started, the work was very productive (see below). The main part of the work at this initial stage was on phase transitions and on the associated structures of thermotropic materials, a new departure for our laboratory with at least a start with flow induced orientability on lyotropics.

THERMOTROPICS

On Choice of Materials; Methodology

We set out to investigate the hierarchical structure in LC forming polymers embracing all phases, comprising crystal, various LC and the isotropic phases and the interrelation of all these structures in the different phases. We realized early that existing materials, at least of the thermotropic variety, were unsuitable for this purpose because some of the phases within the full spectrum are unrealizable. This is largely because they would be in temperature ranges, which are either not accessible, or at which the materials may alter chemically. It appears that the pursuance of the entire subject is being handicapped by this factor world over. We can now state with some confidence that this problem is currently being overcome. This we regard as the main outcome of the work covered by the present report. This has come about through the availability of appropriate copolymers syntheticized by Professor Percec, Cleveland, whose collaboration was secured during my visit to the US reported in my Preliminary Report (March-May 1985). These copolyethers which are more flexible and chemically more stable than the widely studied polyesters, can exist in all the phases of interest within a practicable temperature range.

Another limiting feature in past works, on at least the thermotropic materials, is the small scale of texture in the LC phases preventing direct transfer of knowledge and methodology from the much studied low molecular weight LC materials to polymers. Thanks to the present works this barrier has now been overcome and textures on a much enlarged scale have been obtained raising new expectations.
We expect that both the above improvements (i.e. realizability of all phases from the same material, and enhancement of size and definition of structures) and their combination will prove decisive in the future.

The presently used material is a polyether; a random copolyether of 4,4' - dihydroxy-α-methylstilbene and a 1:1 molar mixture of α, ω - dibromoheptane (PHMS-5-7).

In figure 1- the upper figure shows the chemical structure within a single molecular chain. The flexible spacer occurs randomly as units of either 5 or 7 CH2-groups. This fact, together with the presence of the relatively flexible ether linkages, ensure easily accessible glass, melting and isotropic (clearing) transition temperatures for these thermotropic main-chain LC polymers. In our initial investigations we are studying samples with molecular weights (Mn) between 1800 and ca. 25000.

The lower figure illustrates schematically the types of structure involved. These range from an isotropic liquid (left), through nematic (N), smectic (S) to crystal (C) (right), the sketches being highly schematic. The N,S and C states occur usually as ordered domains which are disoriented with respect to each other, leading to an overall isotropy of the macroscopic sample. These domains can, however, be aligned mechanically (as done in current work) and also by electric or magnetic fields (intended) for purposes of basic studies and applications.

So far the following techniques have been used throughout: Polarizing hot stage optical microscopy, DSC calorimetry, X-ray diffraction.

Guiding principle: calorimetric identification of phase transitions and phase stability intervals, to be correlated with associated light optically identifiable textures (the large end of the structure hierarchy). The latter is then followed by X-ray diffraction which provides information on the molecular organization, i.e. on features at the lower size end of the structure hierarchy.

In what follows some examples will be given of thermograms from each class of experiment with detailed explanations in the figure captions. Without developing the respective themes analytically (this is not possible in brief) the main issues and/or conclusions will then be stated in the main text.

Calorimetric Identification of Phases

Figs. 2,3 show DSC curves of the copolyethers in question, an extract from a much more extensive work from the same material in physically differing starting states. In spite of considerable complexities, particularly in the crystalline phase region (Fig. 3) the existence of crystalline, LC and isotropic phases, together with the corresponding transition points, is clearly identifiable. As a summary of the work so far Fig. 4 displays the various transition points as a function of molecular weight. As
indicated above, the long outstanding need of covering all phases in one and the same material has now been realized. This diagram has become a chart on which future work on this particular subject can now be based. In what follows we shall now be able to select purposefully the phase of interest for any particular investigation.

Of the numerous further facets emerging from the calorimetric works the following few points will be lifted out as of potential consequence for the future.

a) Quenchability. This is important not only in its own right but also because it enables working on the different structures at room temperature (RT). The LC phase can be quenched to RT for all but the lowest MW material. The isotropic phase cannot be quenched under any circumstance; it transforms into LC even on fast cooling.

b) Crystallization can be systematically followed by heating up (annealing) the quenched glassy LC phase.

c) There appears systematically a small peak at $\sim 85^\circ C$ for all samples. This could be a smectic nematic transition (to be examined).

d) There is some system in the complexities of the crystalline transitions not to be enlarged upon here beyond stating that it is the highest temperature peak in a given cluster of peaks. (Fig. 3) which represent the melting of the same crystal form but of differing stability, probably due to different sizes.

As a next stage the light optical and X-ray diffraction manifestations of the different phases, as identified by Figs. 5-8 will be examined.

Light Optical Microscopy

The phase stability scheme as established by DSC (fig. 4) has become fully substantiated light optically with a considerable amount of direct information on hierarchical structure. Conversely, we have now light optical finger prints of the different phases for the work to come.

Figs. 5-8 display a selection from a much more extensive experimental material. In addition to what is said in the captions we can now make the following more general statements based upon such micrographs.

a) Crystallization and crystal growth can now be followed directly from the LC phase whether in situ or after quenching and reheating. This opens the way towards the assessment of the relation between the "domain" structure in the nematic phase and the final crystalline structure, which is one of the main objectives of the whole project (Figs 5,6).
b) We can now juxtapose crystallization from the isotropic (disordered) and nematic (ordered) structures here realized on a conventional time and temperature scale (e.g. Figs. 5, 6). This is an issue which should be of general interest for the solidification of polymers, and beyond, to processing and resulting properties.

c) We observe biphasic effects, i.e. coexistence of isotropic and LC-phase, around the LC-isotropic transition temperature region (Fig. 7) to our knowledge for the first time in thermotropic (as opposed to lyotropic) polymers. This signifies that we must have a bi or multicomponent system which in turn is subject to phase stability criteria such as mutato mutatis, are formulated by Flory's theory for lyotropics. Whether and how this could be attributed to the polydispersity in molecular weights would need investigating. The $T_i$ transitions in Fig. 4 should serve for guidance in this respect. Whatever the ultimate origin of the effect its existence, as now revealed, should be a consequence for thermal and flow behaviour of thermotropics for their processability and for the structure of the solidified final products.

d) The LC "domain" textures can be very large, up to 0.1 mm as in Fig. 8. The significance of having achieved this possibility for the first time in polymers has been referred to earlier. In the past usually only structures in the few μm size range have been seen in thermotropics where the all important disinclination features (one of the main themes in LC studies of small molecules) escape characterisation and study. This has become currently possible, in fact disinclinations of strength 1 have already been identified. Pursuance of this line is basic for comprehending structure hierarchies in LC forming materials. Even more specifically, structures on such large scale open up the possibility of clarifying the long standing issue in LC-s in general, and more recently in polymers in particular, as to the existence of "biaxial nematic" structures. This would correspond to biaxial orientation in local domains (to which the aromatic mesogenes would be particularly prone). If such are truly established, this could link up with microscopic and even macroscopic lamination in extruded objects of thermotropic polyesters as established by Baer and Hiltner. Finally, it is to be remarked that it is highly noteworthy that higher MW materials give larger scale LC textures, a point contrary to experience with true crystalline textures, a feature to be followed up further.

X-ray Diffraction

For this part of the work X-ray diffraction patterns were taken as a function of temperature as guided by the transition temperature diagram (fig. 4). When given the opportunity (in connection with other works in the laboratory) the synchrotron radiation source is also being used with still unforeseeable future potential. To enhance the information value of the diffraction patterns the samples are being oriented whenever this proves feasible. This also links up with flow orientation studies - see below. The explicit experimental material here reported will be on such oriented samples.
While this part of the work is still fragmentary, correspondence with the transition temperature diagram has already been confirmed by X-ray diffraction. Figs. 9, 10. Some of the additional, and possibly totally novel issues arise from patterns such as Fig. 9, the principal features of which are sketched out in Fig. 10a).

12 different reflection groups can be seen, which is surprising for a random copolymer. The reflections have been indexed provisionally assuming an orthorhombic or nearly orthorhombic unit cell. The possible structure is schematically depicted by Fig. 10b. The stilbene mesogenic groups (thick lines) are thought to be regularly packed in layers, giving rise to crystalline diffraction pattern. Stilbene layers are separated by amorphous layers containing the flexible spacers. The short spacers \((-O(CH_2)_{50}^{-}\) are thought to be extended (all-trans form), while the long ones \((-O(CH_3)_70^{-}\) are coiled up. The extended short spacers are thought to be responsible for maintaining the well-defined layer periodicity (reflections up to the 5th layer lines are visible). The measured periodicity of 3.46 nm is very close to the 3.50 nm value calculated on the basis of the model depicted here, assuming standard values for bond lengths and angles. The structure of this kind is rather unique in that the amorphous layers are part of the crystal structure. In particular, full three dimensional crystallographic register is maintained between layers of mesogens separated by amorphous material constituted by the flexible spacers. The currently topical subject of defining the boundary between liquid (smectic) and true crystals (see e.g. Gray and Goodbye \(^{15}\)) is thus given a new test-case possible only in the present type of mesogenic copolymers.

Side Chain LC Polymer

It is part of our objectives with Professor Percec to form a bridge between the two main classes of LC polymers, namely with mesogens in the main chain and as side chains respectively. Samples of both have been obtained, and work is in progress. In the meantime we have noteworthy observations on a side chain LC polymer obtained from a different (industrial) source. The information so far is by X-ray diffraction only.

Here the main chain is \(Si-O_{n}\), and side chain contains \(-O-\bigtriangleup-\bigtriangleup-O-\bigtriangleup-O-\bigtriangleup-CH_3\) mesogenic group attached to the main chain through a \((CH_2)_3\) flexible spacer. The material was obtained in the form of flaky particles of \(0.5 \times 3 \ mm\) size. One diffraction pattern is shown by Fig. 11a. This (and similar) patterns correspond to a highly organized smectic phase).

The main, and possibly totally new, point arising is that the sample has a texture on the scale of the flake (i.e. on a scale of mm-s as revealed by the pronounced orientation in the pattern without using any orienting influence). In fact, a combination of patterns such as in Fig. 11a reveal that the whole flake consists either of one single domain or of a parallel array of such domains, providing an example of a macroscopic element in the possible structure hierarchies.
Some further features are: a) The side chains form layers, the smectic structure elements, where the smectic layer spacing corresponds to a single side chain length. This implies that side chains from neighbouring main chains completely interdigitate. This has precedents but never as clearly demonstrated. b) On externally imposed orientation the layer normals align parallel to the draw direction implying that it is the side chains and not the layers as such (the cases observed so far) which respond to orientation Fig. 11b. When taken together with other known facts this indicates a competition between structure features on different size scales regarding response to external orienting influence.

LYOTROPICS

Orientability of Rod-Like LC Forming Molecules

Work under this heading represents the preliminaries for the investigation on the effect of orientation on LC formation. In its present form it is a continuation of a previous programme in this laboratory, in abeyance for several years, since termination of USAF project. It is centred on the aromatic-heterocyclic polybenzthiazole PBT. In previous works, amongst much else, semi dilute solutions of PBT were oriented and both the process of orientation and subsequent spontaneous disorientation were followed by specially designed optical techniques. At this stage the process of disorientation from the fully aligned state has been taken up again, this being the simplest and as yet unannounced aspect of the subject offering the most tractable link to liquid crystal behaviour in the future. Past works along this line (9,10) established that the disorientation as expressed by the rotational diffusion coefficient ($D_\text{r}$), which is a measure of the orientability of rod-like molecules, proceeds in 2 consecutive stages: a very fast one followed by a slower process. The latter corresponds to the overcoming of the hindering effect due to neighbouring rods, the subject of most previous works (including our own (8)). The study of the former, i.e. the fast process, however, is quite new and was previously believed to be undetectable. However, continuation of these works, with the highly corrosive solvents (methane sulphonylic acid) used at the time (15) proved impracticable, aggravated by the very short time scales involved. In the present revived work we made a new start by transferring it to polyphosphoric acid as a solvent.

Fig. 12 shows results from the newly resumed measurements. The two stages in the reduction of orientation are apparent. The location of the transition between the two regions (marked) is particularly noteworthy: it corresponds to a disorientation of the rods from their initial alignment through 23°. This in turn corresponds to nearest neighbours abutting in the case of local hexagonal packing in the particular concentration involved, which represents the elementary jump in the Brownian rotational motion, the basis of all molecular orientation processes. This correspondence is highly satisfactory and calls for extension to different concentrations and eventually to the liquid crystal forming
range. Nevertheless, the absolute numerical value value of D is far too high for the viscosity of the solvent in question, a point calling for clarification.

ADDENDA

Two further lines of work in this laboratory will be listed, which while presently not on US ERO support, impinge on it subjectwise in a supportive way and which may become an explicit part of the ERO programme in due course.

Orientability of Isolated Collagen Molecules in Solution

Parallel to the above, the orientability of the isolated collagen molecule is being examined using our rather unique 4 roll mill elongational flow technique. Collagen is not only one of the basic biomaterials used in this laboratory, but it is also an excellent model for flexible (wormlike) rods and also nature’s model for hierarchical structure composites. This work on collagen is under Medical Research Council support presently; it interacts with the ERO programme on rigid molecular behaviour both regarding subject matter and methodology. Novel results are being obtained regarding rod flexibility and its dependence on temperature, of potential usefulness for the future, not to be itemized here in detail.

Transition From Crystal to Mesophase in Paraffins

This is an approach of paramount importance having been pursued by Dr. G. Ungar, presently on ERO grant - on his own initiative prior to his joining the ERO programme. It has created, for the first time, a system by which a continuous transition between the crystalline phase in paraffins and the various manifestations of liquid crystallinity in the same materials could be followed experimentally and systematized theoretically. This line of work has been developed by Dr. Ungar throughout his past career including a Science and Engineering Research Council supported stay with us, and is fundamental for the whole subject of ordering of chain molecules. It characterises states of order through entropic and volume terms in their free energy, together with the assessable crystallographic consequences as focussed on the particular case of paraffins. This approach is creating a long awaited unification in a much studied but diffuse field and is being currently incorporated into the ongoing ERO programme.
References


Figure Captions

Fig. 1. Constitution and chemical formula of our thermotropic model polymer (top). Possible phases which can be realized by one and the same compound (bottom).

Fig. 2. DSC heating thermograms of PHMS-5-7 copolymer, $M_w = 12,800$. -- Top curve: solution cast, heating rate 5 deg./min. Bottom curve: quenched to room temperature from the melt (nematic) at 130°C; scanned immediately at 40 deg./min. $T_g$ = glass transition; $T_m$ = crystal melting; $T_{n-m}$ nematic-isotropic transition. The origins of the broad endotherm around 50°C in the solution cast end of the small peak at 87°C in the melt quenched polymer are not clear. The latter may be due to melting of crystals formed during the heating scan, since quenched material was found by X-rays (see Fig 9a) to be amorphous at room temperature. A small and relatively sharp peak of 87°C is present in samples of all molecular weights, both on heating (endotherm) and cooling (exotherm) showing little hysterisis, which suggests that a weak transition other than crystal-nematic might be involved when crystallization is suppressed.

Fig. 3. DSC heating thermogram of PHMS-5-7, $M_n = 12,800$, quenched from 130°C to room temperature and annealed at 68°C for 16 hours. Heating rate 10 deg./min. The combination of annealing experiments at different (higher) temperatures and variable temperature X-ray diffraction confirmed that the multiplicity of endotherms in the 80-110°C range is due to melting of crystals of the same modification but of differing stabilities, presumably due to different crystal sizes. Crystals with dimensions comparable to that of the monomer unit, may in principle lead to such sequence of discrete melting temperatures.

Fig. 4. Calorimetric identification of phase boundaries. Transition temperatures of PHMS-5-7 copolymer as a function of molecular weight as determined by DSC: $T_g$ = glass transition temperature, $T_{ni}$ = nematic-isotropic transition temperature; $T_{m max}$ = maximum melting point of the most stable crystal form, achieved by annealing at low supercooling.

Fig. 5. A sequence of optical micrographs for PHMS-5-7 copolyether ($M_n = 1800$) taken at 2 minute time intervals during crystallization at 60°C from a nematic melt. The weakly birefringent background is a very fine nematic domain texture.

Fig. 6. Sequence of optical micrographs for the same polymer but at a crystallization temperature of 70°C (5 minute intervals). In this case, the melt is optically isotropic, as judged by the black background under crossed polarisers.
Fig. 7. Optical structure near the clearing or isotropisation temperature for PHMS-5-7 with $M_n = 12,800$. Liquid crystal (LC) droplets are present in the isotropic liquid. The clearing transition extends over a temperature range of about 20°C.

Fig. 8. Large scale nematic "domain" textures as familiar in non polymeric LC materials, in this case frozen in within our PHMS-5-7 polymer. In the upper figure ($M_n = 12,800$) the black lines are optical discontinuities between domains which are a consequence of disinclinations and define a texture within the LC material.

In the lower figure for a sample with $M_n = 17,700$ the textures are on an unusually large scale. Here one sees amongst much else many disinclinations of strength 1. These are recognized by the four brushes emanating from each singularity.

Fig. 9. a) X-ray diffraction pattern of PHMS-5-7 in the supercooled oriented nematic state. Fiber was drawn at 120° (nematic) and quenched to the glassy state. Pattern is taken at room temperature, draw axis is vertical. Two pairs of diffuse equatorial arcs are visible, the weaker one corresponding to a Bragg spacing of 1.1nm, and the stronger one to 0.45nm. The sharp rings are due to calcite used as a reference.

b) Same as a) after crystallization above $T_m$ (70°C). Pattern taken at room temperature. The pattern is schematically represented in Fig. 10a). Meridional 002 and 004 reflections are visible, as well as a number of equatorial and off-equatorial reflections, up to the 5th layer lines, the latter being rather unexpected in a random copolymer. The 101 reflections are systematically absent. Note that the degree of orientation is high considering that it is caused entirely by the molecular alignment in the nematic precursor.

c) Same as b) but recorded at 95°C just below the melting point.

Fig. 10 a) Sketch showing sharply defined reflexion such as in Fig. 9a).

b) Possible structure underlying diffraction pattern Fig. 9a) and sketched in Fig. 10a). See main text.
Fig. 11. X-ray diffraction pattern of the polysyloxane with methoxy benzyl benzoate mesogenic side groups linked via an oxypropyl flexible spacer.

a) Flake as received. Seven orders of the 2.0nm smectic layer periodicity are visible. Tri-axial ("single crystal") texture exists on the scale of the collimator width (0.5mm), as revealed by the variable presence of either of the two equatorial diffuse patches, depending on the orientation of the flake.

b) X-ray diffraction pattern of the same side-chain polymer as in a) but after drawing a film of near the top of the smectic temperature range (85°C). Pattern is recorded at room temperature. Draw direction is vertical. The unusual feature of layers preferentially orienting perpendicularly to the draw direction is observed. This anomaly may possibly be linked with the flexible spacer (oxypropyl) being shorter than normally encountered in smectogenic side-chain polymers.

Fig. 12. Disorientation of rigid rod PBT in 0.5% (semi dilute) solution of polyphosphoric acid from fully aligned state attained by appropriate shear flow. The slope is a measure of rotational diffusion coefficient. The reduction of initial slope at (dis)orientation angle 23° corresponds to onset of mutual interference of nearest neighbour rods.
In the light of the foregoing the scene is now clearly set. The new materials being synthetized by Professor Percec, Cleveland, have proved to be outstanding model materials for a comprehensive study of thermotropic polymers in the widest generality and in particular for the study of structure hierarchies embracing all mesomorphic and crystal phases, for the first time in the liquid crystal polymer field. Specifically this is to include also the influence of molecular weight, heat treatment and orientation. The present first period has laid the groundwork and has established the all vital collaboration with Professor Percec. The exploitation is to follow with hopefully wide ranging consequences.

Flow induced orientation on rigid rod molecules in the lyotropic state is to be extended along the lines presently initiated. Extension of this work to thermotropics will rely on availability of Professor Percec's material in sufficient quantity, which is hopefully anticipated once we can identify the material most suited for this purpose. The latter we propose to do in the near future. Till then flow induced orientation work on the same materials will be initiated in the solution state.

The actual work started 1st October 1985, the state at which the Staff Members on ERO Grant, Drs G. Ungar and A.J. Owen, were engaged. The latter could not be done earlier, hence the gap between the period covered by the Preliminary Report (March - May 1985) and the present during which no work has been carried out. The previous Preliminary Report covered action preparatory to the actual Research Programme.
MAIN CHAIN LIQUID CRYSTAL FORMING COPOLYMERS WITH ETHER LINKAGE

PHMS-5-7 synthesised by V. Percec

Linear macromolecule

\[
\begin{array}{c}
\text{MESOGENIC UNIT (rigid rod)} \\
\text{ETHER LINKAGE} \\
\text{FLEXIBLE SPACER}
\end{array}
\]

\[
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{C} \quad \text{C} \\
\text{CH}_3
\end{array} \right] \\
\begin{array}{c}
\text{O} \\
\{ \text{CH}_2 \}_n \\
n = 5 \text{ or } 7
\end{array}
\]

Schematic structure of various phases

Isotropic Phase | Nematic Domain | Smectic Domain | Crystal
---|---|---|---

Fig. I
$M_n = 12,800$
annealed at 68°C 16 hours

Fig. 3
Growth of crystallites from a nematic melt at 60°C

PHMS-5-7 (Mn = 1800)
Growth of crystallites from an isotropic melt at 70°C
PHMS-5-7 (Mn = 12,800)
Biphasic separation at 156°C
Texture of quenched nematic melt showing disclinations and brushes.
Fig. 12

RELAXATION OF PBT/PPA
0.5% 32 IV.

ONSET OF ROD INTERACTIONS
ORIENTATION ANGLE--23

TIME (MS) 10
END DATE
FILMED 8-88
DTIC