

AD-A193 566

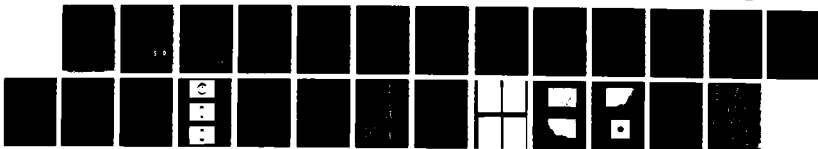
HIERACHICAL STRUCTURE IN POLYMERIC SOLIDS AND ITS
INFLUENCE ON PROPERTIES(U) BRISTOL UNIV (ENGLAND)
A KELLER MAR 87 DAJA45-85-C-0004

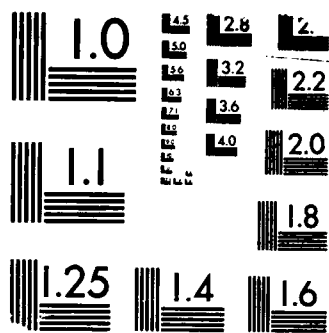
1/1

UNCLASSIFIED

F/G 7/6

NL





MICROCOPY RESOLUTION TEST CHART
BUREAU OF STANDARDS-1963-A

AD-A193 566

HIERARCHICAL STRUCTURE IN POLYMERIC SOLIDS AND ITS INFLUENCE ON PROPERTIES

Investigator: A. Keller

Contractor: Department of the U.S. Army, ERO

Contract Number: DAJA45-85-C-0004

4th Periodic Report*

October 1986 - March 1987

The Research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. ~~This report is intended only for the internal management use of the Contractor and the U.S. Government.~~

*3rd on work performed

DTIC
ELECTE
APR 27 1988
S H D

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

88 4 27 012

SUMMARY

Work was again centred on the family of mesogenic polyethers (synthesized by Professor Percec, Cleveland, USA) which are the most ideal model substances for liquid crystal polymers to date in aid of the exploration of polymeric structure hierarchy. Following leads given by results during the preceding period advances were made along two directions.

Improved orientation processes have been arrived at which have greatly helped the exploration of the fine scale end of the structure hierarchy. This embraces the identification of different packing modes of the mesogen-spacer sequence constituting these polymers with implications for the whole wide family of substances. In particular, the stacking mode determined by the 3 dimensional contact of mesogens only (our new 'chess board' structure) became clearly distinct from the more traditional layer stacking with potentially wide ranging consequences, for relationship between molecular composition, molecular stacking, morphology and macroscopic properties.

The second main thrust was towards the establishment towards a unified phase diagram linking the lyotropic and thermotropic state including morphology. The practical problems associated with this unique possibility (recognized during the preceding period) have now been overcome and the continuity between the lyotropic and thermotropic behaviour has just been established with the consequences arising currently being explored. Amongst the latter emerging are e.g. the mesogen-spacer length ratios, the co- v. homo-polymer nature of the chain, greatly influencing both phase diagram and morphology. In the course of it all, the gel state with its manifold potential has come in evidence.

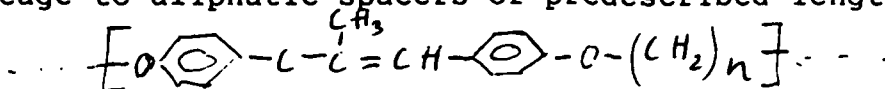


Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By <i>perform 50</i>	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
<i>A-1</i>	

105 1

INTRODUCTION

Work during the present period has centred again on the new polymeric liquid crystal model materials which have become available thanks to the cooperation of Professor V. Percec, Case Western Reserve University, Cleveland, USA. As laid out previously these materials are polyethers with styrene as mesogenic unit linked through ether linkage to aliphatic spacers of predescribed length



where n is a variable (5,7,9, or 11, homopolymers or alternatively 5 and 7 or 9 and 11, copolymers). As stated previously these materials are ideal models for liquid crystal forming materials as, in contrast to most others being studied currently, they can exist in all states, isotropic liquid, liquid crystal, true crystal also coupled with the glassy state both as single component (thermotropic) and bicomponent (lyotropic) materials.

Advances, during the previous period have set the objectives for the present. These comprise two main lines. One is the establishment of the continuity between the lyotropic and thermotropic states, together with associated structure hierarchies and the other is the exploration of mesogen - spacer packing schemes both opportunities uniquely offered by their materials. As stated previously we expect these two lines to reinforce each other in quest of comprehensive knowledge, control over processing and properties.

In what follows the mesogen-spacer packing subject will be covered first as it has made most headway. Reporting of the work on phase diagrams, passing through an induction period due to change in staffing is to follow.

I. MESOGEN - SPACER PACKING:

The underlying issue arises from the two component, mesogen-spacer, nature of the molecule, the mutual arrangements of which represent the fine scale end of the structure hierarchy. The issues arising are of general validity for this class of material pursued primarily by X-ray diffraction.

The Drawing Process - Sample Preparation - Diffraction Pattern

For this objective the material had to be oriented. While this served the primary purpose of obtaining as well defined X-ray patterns as possible, it also proved valuable for identifying the most efficient drawing method. Even if only on a small scale, it became apparent that substantial drawing stress is required for good final orientation and this needs to be maintained during the full drawing process. To achieve this, drawing was conducted not in the molten state proper but on heating the frozen nematic sample just above its glass transition temperature. Here, not only is the material more viscous, but, chiefly it is also strain hardened by stress-induced crystallization, itself promoted by the drawing process. While pointing to routes of processing of these and similar materials the present purpose of high quality diffraction patterns surpassing those in previous attempts has been achieved (see e.g. Figs 2,3).

The wealth of reflexions emerging has led to correspondingly enhanced information content which has enabled us to place issues on the map which previously would have been unapproachable. More specifically, the materials in the form considered span both liquid crystal and true crystal, and in particular, the border area between the two; explicitly, the interface between 2 and 3 dimensional order. As will be shown, this can involve different modes of coupling between stiff and flexible regions.

'Chess board' v Layer Structure and Consequences

As recognized previously but firmed up during the present period, consecutive mesogen and spacers have differing cross-sectional areas, hence both simultaneously cannot fill space optimally. The whole subject area revolves on the optimization of these two conflicting requirements.

Specifically, the two main alternatives are:

1) If the mesogens themselves pack as closely as they can this will lead to a layer structure but there will be much empty space between spacer chains. (Fig.6). This is a source of disorder which features in successive structure hierarchies: in the present case it is manifest as an intra molecular - intra lattice (or quasi-lattice) feature, while in conventional semi-crystalline polymers it is a superlattice feature in the form of amorphous-crystalline layer structures.

2) The system abandons best mesogen packing and reaches a compromise between mesogen interactions and spacer accommodation. This leads to a three dimensionally alternating interdigitating structure (Fig.5) indicated by X-ray diffraction patterns such as Fig.2. It will be termed 'Chess board' structure.

In the light of the foregoing the principal consequences (recognized during the present period) of 1) and 2) above are as follows. In the layer structure (1) stiff and flexible spacers are coupled in series, while in the 'chess board' structure as presently envisaged (2) there is continuous contact between the stiff units with the spacers, which feature as occlusions corresponding more to a parallel coupled stiff-flexible structure. The former should give a low crystal modulus, elastic up to high strains, while the latter the converse, i.e. high crystal stiffness but low elastic limit. The potential for utilizing these features through appropriate design of lattices (a hierarchy design between the chemical and morphological levels) for macroscopic mechanical properties will be apparent. This has emerged during the present crystallographic work, which otherwise has concentrated on state of order rather than properties.

From the lattice order point of view the 'chess board' structure (2) is always 3 dimensional containing variable amount of conformational disorder.

In the layer structure (1) the order can be between 2 and 3 dimensional. On the first level the ordering is within the layer, which is intrinsically 2 dimensional and, it is the stacking of the layer which leads eventually to full 3 dimensionality. There are two stages in the achievement of the latter. The first is the regularity of the stacking itself, the second the establishment of the long range positional order uniquely relating any point in one layer to any other within a different layer.

The above newly arising possibilities have been already perceived during the previous period. However, sufficiently high quality diffraction data and computational molecular modelling have been called for to determine the unit cell and symmetry elements required for substantiations which has then led to further new recognitions. In what follows a brief survey on diffraction and on computational modelling will be presented with subsequent application to some specific cases.

The Diffraction method; Information Provided

The principal signposts provided by the diffraction patterns will be briefly defined together with their utilisation for the present mesogen-spacer structure issue.

i) Meridional reflexions

These are the fingerprints distinguishing between layer and 'chess-board' structures, according to whether they correspond to full (Fig.3) or half (Fig.2) chemical repeat periods (mesogen plus spacer) respectively. In case of layers the quality of the reflexions (width, number of orders) together with the exact numerical value of the spacing defines the layer stacking. Some such values are being quoted in Tables I and II.

ii) Equatorial reflexions

These give the structure within the layer which can range from uncorrelated parallel chains to high degree of order (Fig.3).

iii) Row lines

The existence of off-meridional row lines (Fig.2,3) provides direct evidence for transmission of order from one layer to the next. They have become apparent thanks to our unique polymers and new fibre drawing method.

Texture versus Structure

By conventional crystallographic interpretation within an X-ray fibre diagram the fibre axis coincides with a principal crystal axis which in polymers is usually the chain direction. However, this is only the simplest case of a texture pattern. In the more general situation there can be a whole structure hierarchy between the basic lattice and more complex arrangements thereof, all cylindrically averaged. In the present work this issue has come up in terms of inclined structures which is manifest not only through splitting of meridional reflexions (referred to previously) but also through skewing of layer lines (Fig.2).

Molecular Modelling

Conformational possibilities and associated molecular dimensions were tested to provide comparisons with the X-ray diffraction patterns. It happens that these considerations have led to the realization of the existence of further sources of lattice disorder as yet to be explored.

A computerized molecular graphics package was utilized to obtain atomic coordinates and generate models. Literature data (both experimental and theoretical) on nearest structural entities were used for bond angles and lengths. It ought to be realised that even what we in this study call homopolymers are strictly speaking random and atactic copolymers involving several degrees of freedom in the orientation and configuration of the mesogens. This touches upon the fundamental issue of crystallisation of "noncrystallizable" atactic polymers and random copolymers. The inherent chemical disorder is, on the other hand, instrumental in bringing about liquid crystallinity by depressing the crystal melting point (cf. stilbene vs methylstilbene derivatives). Some such sources of disorder will be specified in what follows.

With reference to Fig.7 it is clear that (a) the methyl group can be attached either to the a or to the a' carbon atoms, which introduces a head-to-head/head-to-tail type of disorder. (b) Since the methylstilbene molecule is highly non-planar, the methyl group can protrude above or below the plane of the paper (configurations denoted u and d in Table I), the atactic polymer involving a random sequence of such units. The third source of disorder (c) involves the rotation around the Ar-O bond whose high energy due to the clashing hydrogen atoms warrants it to be regarded, to some degree, as configurational rather than conformational. Four such possible configurations are depicted in Fig 7. Extensive investigation of molecular models (some examples of HMS-5 trimers are shown in Fig.9, for monomer see Fig.8) reveal that, with odd-numbered spacers in all-trans conformation, only configurations K and L lead to extended or nearly extended chain conformations, while the presence of R or S types invariably lead to severely bent and thus non-crystallisable chains. Such bent chains cannot participate in nematic phase formation either, and here the flexible spacer, with its connective capability, may prove to be the crucial constituent.

In Table I two-monomer-unit lengths, as calculated, are shown for different configurations of PHMS-5. Measured two-monomer repeat distances in forms A, B and C (for these forms see later) of this homopolymer are listed at the bottom of Table I. Since the latter all coincide or even somewhat exceed the calculated value for the most extended configuration, we conclude that the relatively short $-O(CH_2)_5O-$ spacer is in its all-extended conformation in all crystal forms. This was an important conclusion for establishing the structure schemes announced in the foregoing. Further, as will be apparent below, departures from it, now readily identifiable in polymers 7 and 9 and in copolymers 5,7 acquires special significance. Finally, the close similarity between extended monomers, here firmed up quantitatively, offers new pointers for future works both on structure evaluation (order-disorder) and on synthesis.

Application to a specific structure sequence

The structure scheme announced above is to be illustrated by a specific structure sequence observed in homopolymers 5 and 7 together with further implications arising.

On first quenching of the pure oriented filament we have a glassy nematic structure (such as fig.17 in Report May-Sept. 1986). Above the glass transition (T_g , 40°C) crystallisation in a form, we term A,

takes place. In the quiescent state crystallization is slow and the resulting order is poor, displaying only three meridional reflections. It is at this stage that mechanical drawing just above T_g greatly increases crystallization rate and the order arising; numerous reflections along more than twenty layer lines appear. The fibre repeat here is two monomer units long (Fig. 1) and the overall arrangement is of the poorly ordered layer type.

The most pertinent feature for the present is the small lateral spread of the first meridional compared to the much larger spread of the second. This phenomenon (known as "fanning") indicates undulation of lattice planes (fig. 4) with the interplanar spacing highly uniform in the fibre direction as indicated by the narrow meridional line width throughout. Thus intramolecular crystallinity, induced by drawing, is highly developed, but intermolecular register is still poor, a state of order somewhat intermediate between the nematic and crystal proper.

On further heating (to about 100°C) structure A transforms first into a structure we term B (Fig. 2) which in turn, at still higher temperatures ($120-130^\circ\text{C}$), transforms into as yet another structure to be termed C (fig. 3). Form B we identify as the intermeshed or 'chess board' structure (already introduced in general terms - (see Fig. 5) while form C emerges to be a layer structure which is more ordered and altogether different from A.

For the layered C the unit cell and space group could now be determined (Fig. 6). Thanks to this and with the combination of diffraction and molecular modelling data a certain amount of highly relevant information could be obtained on molecular conformation and packing. The lateral unit cell parameters a and b are 7.62A and 6.30A respectively, while the fibre period c varies from polymer to polymer as listed in Table II.

There are two chains, each with two monomer units, in a cell. As already mentioned, the c-dimension for PHMS-5 coincides with the calculated 2-monomer length of the extended lowest energy conformation. In all other polymers the observed c-spacing is significantly shorter (cf. 4th column in Table II) and the corresponding crystal densities are higher (5th column). We attribute this shortening to coiling up of flexible spacers which enables an increase in density of the spacer layer. This coiling up requires the introduction of gauche bonds, hence a departure from the lowest energy chain conformation. Hence, there will be an energy balance between the opposing requirements of chain conformation and space filling. It appears from our results that for shorter spacers the chain conformation will be optimal (extended) at the expense of space filling (density), while for longer spacers progressively the converse will hold. Simple calculation shows that the spacer layer density in PHMS-5 is 0.765g/cm^3 , that is lower than the density of liquid paraffins (0.86g/cm^3). Such low density is imposed on the spacer layer by the packing requirement of the mesogens with their large cross-sectional area.

The layered form C is orthorhombic with the space group Pnam. The packing arrangement is schematically drawn in Fig. 6 with the parallelepipeds symbolizing the mesogens. Note that the centres of the spacers lie on the mirror planes that are normal to the molecules. Also note that the mesogens are not parallel to their nearest neighbours within the same layer.

It is instructive to compare structures B and C regarding width and intensities of reflections. In B meridionals and off-meridionals are sharper and retain reasonable high intensities up to large diffraction angles (spacings down to 1.4Å). On the other hand in the layered form (C) these reflections are broad with appreciable intensities only to relatively lower angles (spacings down to 5Å). This is a consequence of the full three dimensional order in B as opposed to the quasi order of layer stacking in C.

The better developed 3 dimensional order in samples formed at lower temperatures is remarkable, and is a consequence of the special structure forming capabilities of the mesogen-flexible spacer combination in this family of chain molecules. The fact that transition B C is endothermic strongly indicates that at the appropriate temperature structure B is indeed the stable one.

It is to be noted further that the more perfect structure B arises through a less perfect structure (A) directly from the glass. This points to the fact that overall molecular orderings and transformations rather than nucleated crystal growth is involved, and further that the line broadenings, where present, are due to correlational disorders, rather than the limited crystal size.

The 'chess board' structure has so far been observed in homopolymers 5 and 7; we could not obtain it in homopolymer 9. This is consistent with the nature of the model, namely that there is a latitude for space filling and chain extension within the low density domains accommodating the flexible spacer. The size of these domains is determined by the mesogen packing only which in the present case is consistent with fully extended (i.e. all trans) spacer configuration for polymer 5 and allows for contracted and correspondingly less regular (containing gauche sequences) configuration for polymer 7. Supporting this model is the finding that fibre periodicity in polymers 5 and 7 are identical (10.1Å), which is the expectation from a structure that entirely rests on a 3d network of mutually interacting rigid mesogens, with the flexible spacers merely filling the voids between them. Since only layered structures are found in polymer 9, it can only be surmised that spacer 9 can no longer be accommodated in the voids. Clearly, all this offers a profitable further avenue to explore the effect of mesogen-spacer ratio on the nature of the sublamellar microstructure.

A note on copolymers

It was established during a previous period, that copolymers in the layer form stack as appropriate to the extended shorter spacer (e.g. 5 in polymer 5,7), the longer spacer being accommodated in a disordered form. This has been verified further throughout ongoing work, bearing out a structure principle for inhomogeneous mesogen-flexible spacer polymer chains. We abstain here from separate documentation which would involve laying out also various tilt modes (see last report) but refer to one entry in Table I for polymer 5,7. While broadly conforming to polymer 5, this shows the additional effect of actual shortening of the spacing below that of pure 5, with the implication of further disordering of the interlayer, which rather remarkably, is in aid of achieving a density which is higher than either for pure 7 or 5.

II LYOTROPIC BEHAVIOUR - MORPHOLOGY - PHASE DIAGRAM

As stated in previous report the present polyethers are soluble and can exist as lyotropic liquid crystals, as well as can form solution grown crystals. This opens the unique possibility of combining the full phase behaviour - both lyotropic, thermotropic liquid crystals and true crystals including the corresponding morphology for the first time in one and the same system. This possibility became apparent during the last period when it was probed in selected cases, leading to a schematic phase diagram (Fig. 2 there) necessarily valid in essence, but requiring mapping regards particulars. Presently considerable effort has been expended to identify the appropriate polymer-solvent pairs through which the lyotropic - thermotropic behaviour could be continuously linked also with access to the morphology. After several starts this objective is on the way to be achieved. Several somewhat conflicting requirements needed to be satisfied: i) Readily identifiable morphologies ii) Large difference between isotropization (T_i) and melting (T_m) temperatures for ease of mapping of coexistence boundaries, iii) High boiling solvent to cover the full concentration range from dilute up to near 100% at atmospheric pressure. It was found that there was no simple system to satisfy i) ii) and iii) simultaneously while ensuring experimental convenience such as is desirable for first ever mapping. Homopolymers in low boiling solvent were the best for the study of morphology but were less suited for following up the phase diagram. Even so, morphological work has continued within these temporary restrictions to be briefly reported first.

Morphology

The homopolymer 5 was used in commercial (mixture of ortho and para) and pure para xylene (there were notable differences between the two not to be enlarged upon here) at the high dilution end of the phase diagram. The principal innovation since the last report was the use of scanning microscopy combined with a preparation method newly applied to these systems in order to reveal the 3 dimensional features of the structure hierarchy and this in combination with optical and transmission electron microscopy.

The first observable features at high dilutions were representative oval shaped 3-dimensional objects with smooth outlines, but central clefts (Fig. 10). These rounded objects are characteristic hallmarks of liquid-liquid phase separation representing the solute-rich phase. The ovaloid, spindle like shape has precedents in the old (non polymeric) liquid crystal literature now practically in oblivion, where they were termed 'tactoids'. (H. Zocher and K. Jacobsohn, Kolloidchemische Beihefte, volume XXVIII, No. 6, p.11, 1929). We therefore maintain that we have verified both the liquid-liquid phase separation and possibly also the liquid crystalline nature of the concentrated phase in terms of external shapes, also reviving a long forgotten aspects of the subject. Incidentally, these shapes should represent structural constituents of the final solidified materials on the appropriate level of the structure hierarchy.

Corresponding transmission electron microscopy, where the objects were small enough to permit some transmission, revealed a layering like substructure with a thinner central area corresponding to the cleft seen by SEM (Fig. 11). This strongly suggests that crystallization has taken place in the dispersed phase before the concentration was increased on drying, setting the external shape of the 'tactoids' which

then buckles or breaks open as their interior becomes depleted of polymer (quite recently observed in isotropic polymer phase separation of polyethylene (P. Shaaf, B. Lotz and J.C. Wittmann, *Polymer*, 28, 177 (1987))).

The polymer content in the dilute phase at this low overall polymer concentration will be very slight and difficult to detect electronmicroscopically after crystallization. Nevertheless it has become apparent as exceedingly thin isolated layers adhering to the tactoids (arrowed in Fig. 12). They gave clearly defined electron diffraction patterns (Fig. 13) identifiable with the c axis view of homopolymer 5, the lattice of which is known precisely from the above X-ray diffraction work on fibres. Such electron diffraction patterns were observed in the previous report but these, amongst the multitude of structures seen could not as yet be identified with the visible image to any degree of certainty. This identification has presently been achieved, and with it the basic chain folded crystallization by the familiar argumentation to our knowledge, for the first time in a mesogen-spacer system.

The phase diagram

This was pursued by recording the onset of turbidity coupled with lightening up of the field between crossed polaroids. For reasons stated earlier we switched to copolymer 5,7 sacrificing some distinctness of the optically visible morphology. Beyond a minimal polymer concentration the phase boundary liquid-liquid crystal, by our anisotropic turbidity diagnosis becomes rather 'flat' rising only slowly with concentration (c) (fig. 14). With xylene we could not go beyond $c = 40\%$ without resorting to the complication of a sealed (pressurized system) as the solvent boiling point was being approached.

In what follows we turned to another solvent, diethylphthalate, which had a high enough boiling point for T_i of the pure thermotropic system (150°C) to be reached. A new start with this solvent was made. Results emerging at the time of writing now, for the first time, connect the lyotropic and thermotropic phases in a single phase diagram (Fig. 15). While still incomplete, the continuity of the T_i v. c curve is apparent. Resemblance to the idealized schematics is not immediately obvious. Nevertheless we expect the 'chimney' to become apparent once the T_m v. c curve is also mapped. It is clear, even at this stage, that such a chimney is much shifted to high c -s and is likely to be very broad. This is in line with the only existing theoretical expectation (R.S. Werbowyl and D.G. Gray, *Macromolecules* 69, 13 (1980)) when introducing flexible spacers into rigid rod molecules. It is for rigid molecules for which the shape such as in Fig. 2 of previous report is expected to hold. We see therefore that in addition to connect thermotropic and lyotropic phases regarding phase diagram, we should also be able to test for the effect of flexible spacers and compare with predictions such as exist to date.

A note on liquid crystal gels

For the record, we observed the lyotropic system to gel under specific circumstances. Gels in liquid crystal systems have been reported previously mostly for biological molecules, but in the present instance we can place them in the context of the phase diagram. In view of extensive ongoing work on gels from the more common isotropic polymer solutions based on binary phase behaviour in our laboratory we hopefully anticipate the gelation of lyotropic polymers to fall within

a wider unifying scheme with planned control over the gelation. Gels represent a unique state of matter with importance for technological processing and products such as e.g. the gel spinning route for ultrastrong polyethylene fibres. We believe that our current experiments are likely to offer similar opportunity with the added advantages associated with the liquid crystalline state.

RESEARCH PLANS

Results of the present period have clearly set the scene for the continuation. This will be again on Professor Percec's (Cleveland) unique family of materials of which further new members have been promised.

The newly firmed up mesogen-spacer stacking scheme will be pursued extending it to other spacer lengths. This is to test the scheme's limits of validity, in terms of mesogen-spacer ratio, including the linking up of this family of materials with those containing no spacers at all and to explore the consequences of the newly uncovered modes of mesogen-spacer coupling, in terms of stress response.

The main thrust is planned towards the exploitation of the newly arising possibility of linking the lyotropic and thermotropic state by a unified phase diagram. The possibility was recognized during the past period the practicalities established during the present (now reported), and we believe the scene is set for a concentrated attack on it in the immediate future. The possibilities are manifold with many consequences still unforeseeable. These include the verification of existing theoretical (thermodynamic) conceptions and pointers towards new ones in particular regards the influence of flexible spacers. Morphologically it opens up new horizons for mapping out structure hierarchies on a wider front than possible before, promising at the same time to provide pointers to new routes of processing (e.g. choice between wet and melt processing) as a function of molecular composition and resulting properties. In all these respects the newly uncovered gel state will receive further attention (possibility of gel spinning ?!).

With new knowledge and experience acquired return to the original orientation objective will be considered, when and as sufficient amounts of material of this exceptionally suitable model substance becomes available.

TABLE I

Calculated 2 monomer repeat (d) for Polymer 5 (PHMS-5) for
different conformations

Conformation		d (A)
$K_d K_d$	extended	37.8
$K_d K_u$	"	37.9
$L_d L_d$	"	36.7
$L_d L_u$	"	36.6
$K_d L_d$	"	37.4
$K_d L_u$	"	37.4
<hr/>		
$K_d S_d$	bent	36.8
$K_d S_u$	"	36.7
$K_d S_d$	"	35.8
$K_d S_u$	"	35.8
$S_d S_d$	"	35.9
$S_d S_u$	"	35.9

measured 2-monomer repeat for PHMS-5

form A: 40.1A
 "chess-board" (form B): 40.4A
 layered orthorhombic (form C): 37.8A

TABLE II
Parameters for Form C

	Measured c-spacing (A)	calc. range of 2-monomer repeat distance for extended conformations.	shortening w.r. most extended conform.(A)	crystal density (gcm ⁻³)
PHMS-5	37.8	36.6 - 37.9	-0.1	1.05
PHMS-7	37.7	41.7 - 43.0	-5.3	
PHMS-9	42.0	46.8 - 48.1	-6.1	1.15
PHMS-5,7	34.6	36.6 - 37.9)*	-3.3*	1.21

* calculated as PHMS-5

FIGURE CAPTIONS

- Fig. 1 X-ray diffraction photograph of stress-crystallized PHMS-7 fibre, crystal form A. Draw direction vertical; the rings originate from a calibration substance.
- Fig. 2 X-ray diffraction pattern of the same PHMS-7 fibre as in Fig. 1 but after annealing at 105°C, crystal form B ("chess board").
- Fig. 3 X-ray diffraction pattern of the same PHMS-7 fibre of Figs. 1 and 2 after annealing at 132°C, crystal form C (orthorhombic layer form). Note the absence of higher layer-line reflections.
- Fig. 4 "Fanning" of meridional reflections observed in form A (fig. 1) indicates undulation of real lattice planes normal to the fibre axis.
- Fig. 5 Schematic two-dimensional representation of the "chess-board" structure (B). Rectangles symbolise the mesogen moieties. Note that these rectangles are in contact and their arrangement determines the 3 dimensional lattice containing the flexible spacers as low density 'occlusions'.
- Fig. 6 Crystal form (layered) C, space group Pnam; unit cell drawn schematically for PHMS-5 in ab and ac projections. The parallelepipeds denote the mesogen moieties. All dimensions are drawn to scale.
- Fig. 7 Definition of mesogen conformations K, L, R and S.
- Fig. 8 Lowest energy monomer conformation (molecular graphics, parameters taken from experimental and theoretical literature data on analogous compounds).
- Fig. 9 Molecular graphics models of three selected conformations of a HMS-5 trimer.
- Fig. 10 Ellipsoidal entities (with central clefts) formed on cooling homopolymer 5 in a 0.05% solution of xylene. These have the principal hallmarks of being the result of lyotropic liquid-liquid crystal phase separation. Scanning electron micrograph after freeze drying.
- Fig. 11 Same as in Fig. 10 but as seen in the transmission electron microscope. It also reveals a layer substructure possibly due to the formation of true crystals on cooling and solvent evaporation.
- Fig. 12. Separate thin layer type entity adhering to a large ellipsoidal object, assumed to form from the dilute phase after liquid-liquid phase separation. Transmission electron micrograph.
- Fig. 13. Electron diffraction pattern of a layer as in Fig. 12 identifying the latter as a chain folded single crystal.

Fig. 14. Phase diagram showing the isotropic - anisotropic (T_i) coexistence curve for the system copolymer 5-7 and xylene up to 40% polymer concentration.

Fig. 15. Phase diagram showing the isotropic - anisotropic (T_i) coexistence curve for the system copolymer 5-7 and diethylphthalate linking up with thermotropic behaviour (100% polymer).

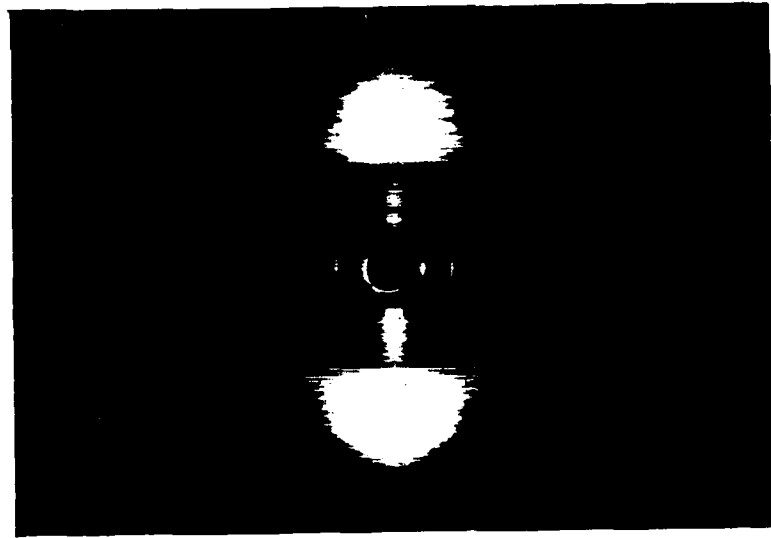


Fig.1

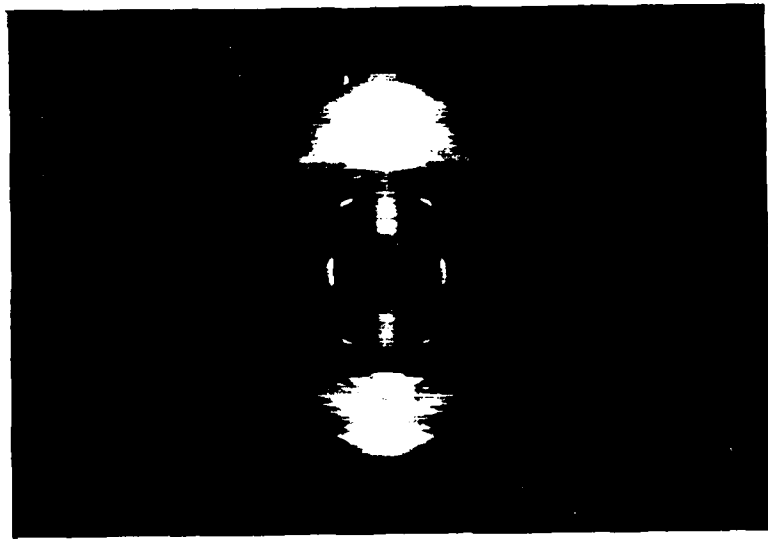


Fig.2

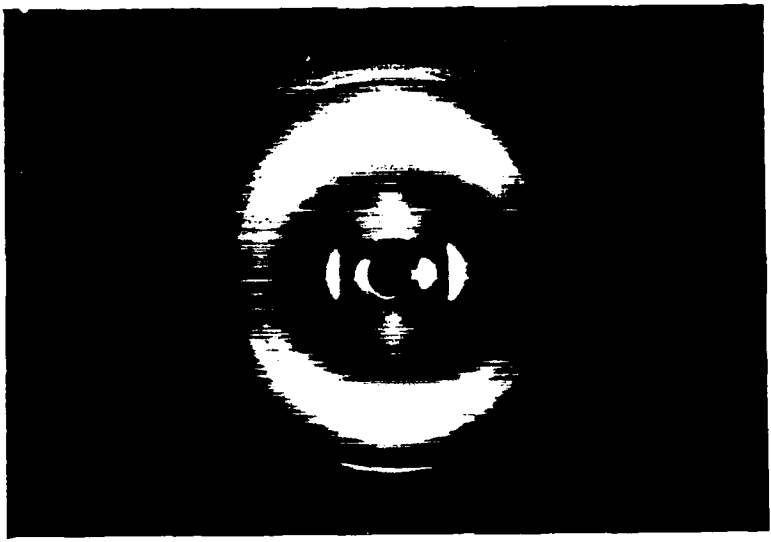


Fig.3

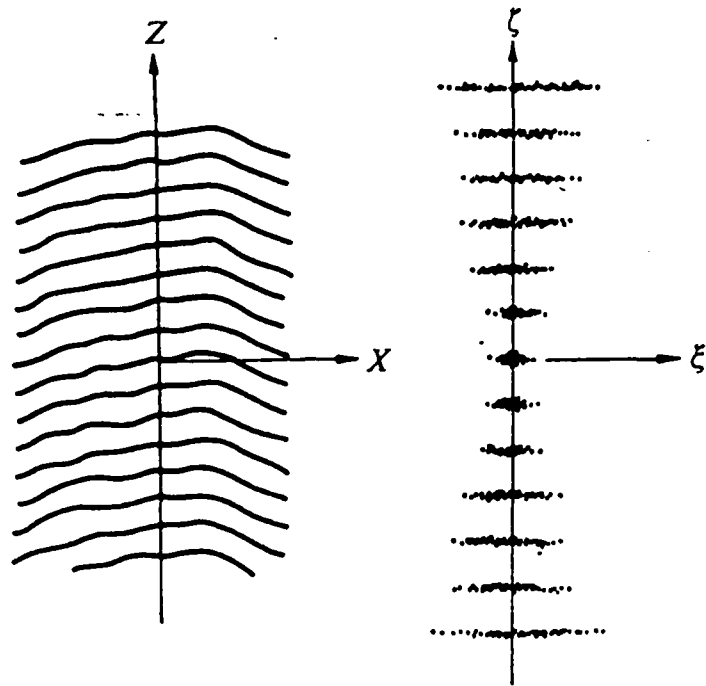


Fig. 4

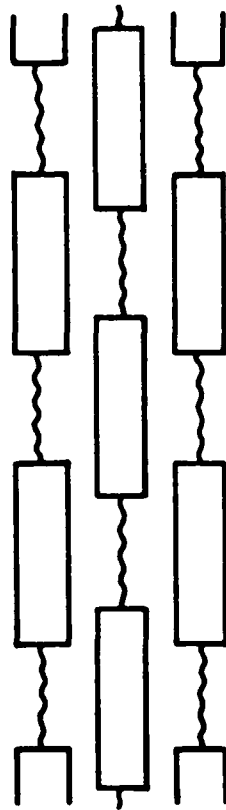


Fig. 5
Form B

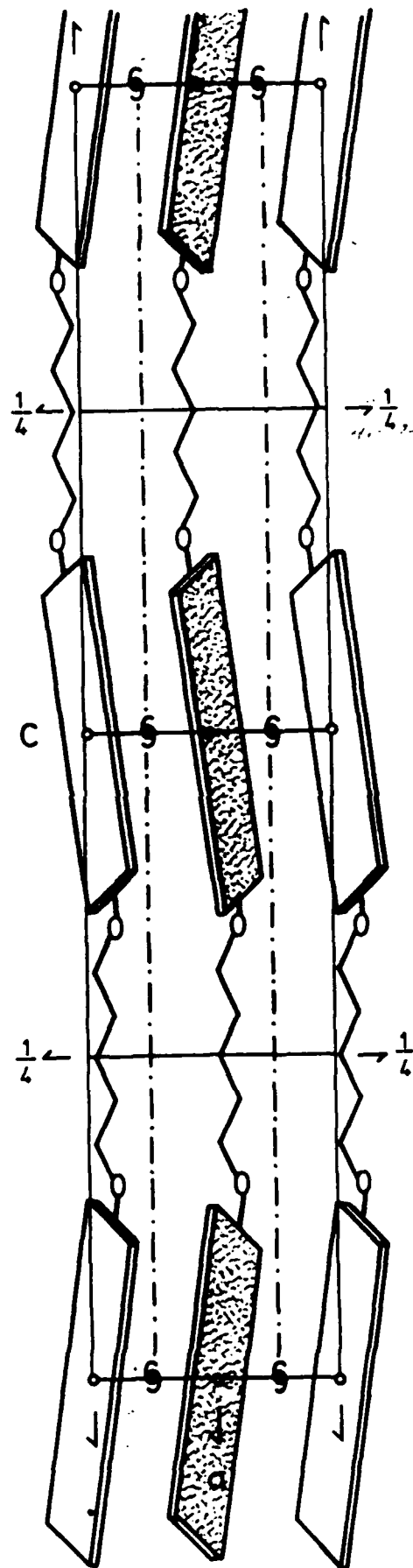
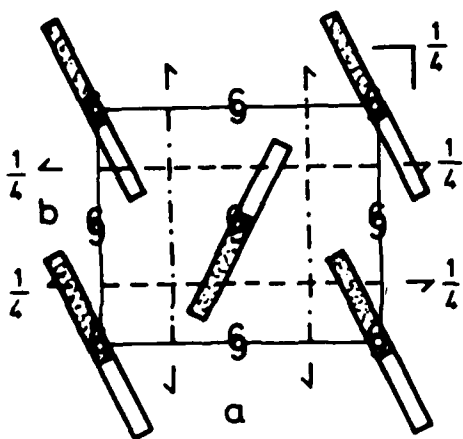


FIG. 6

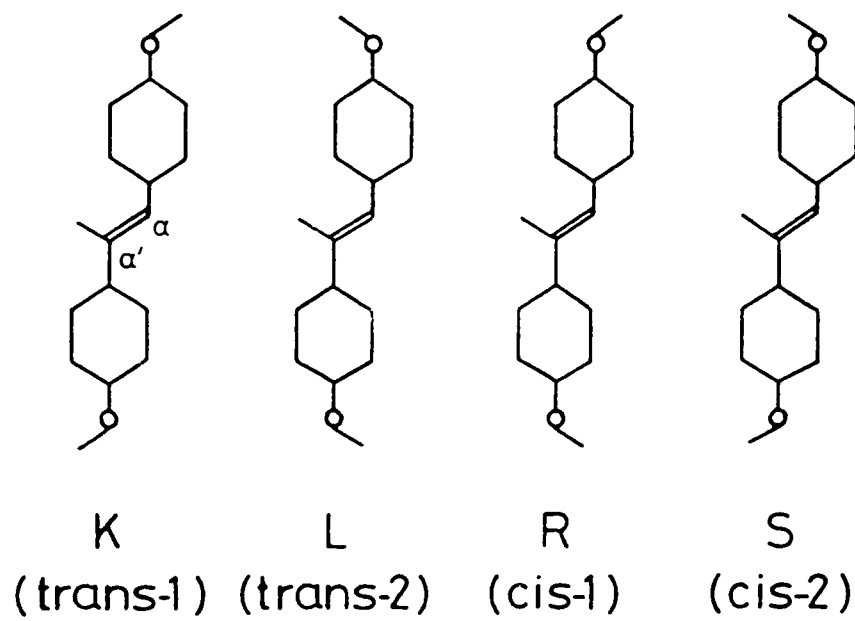


Fig.7

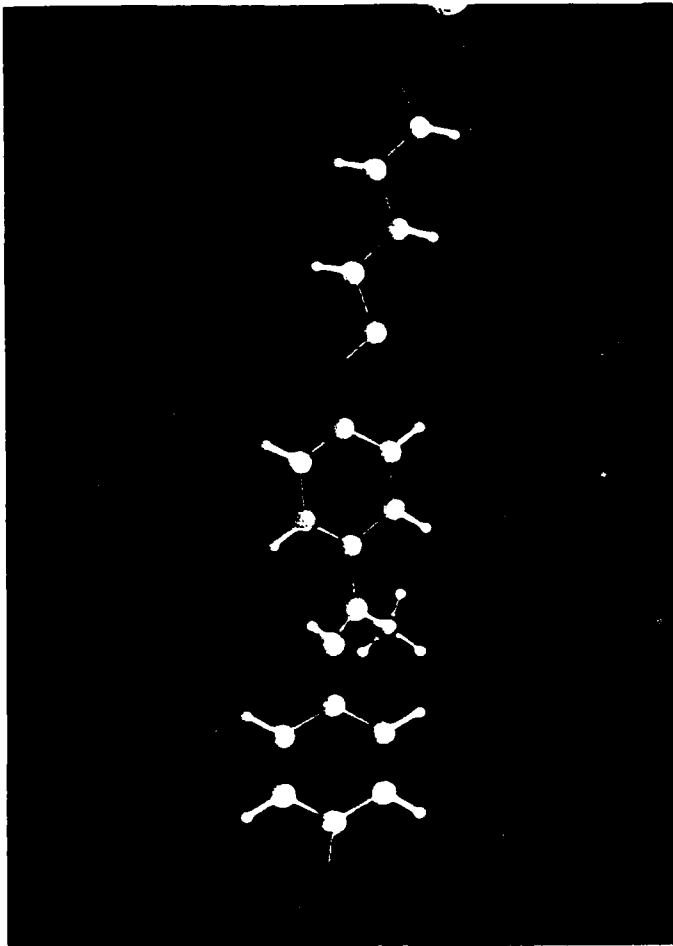


Fig. 8

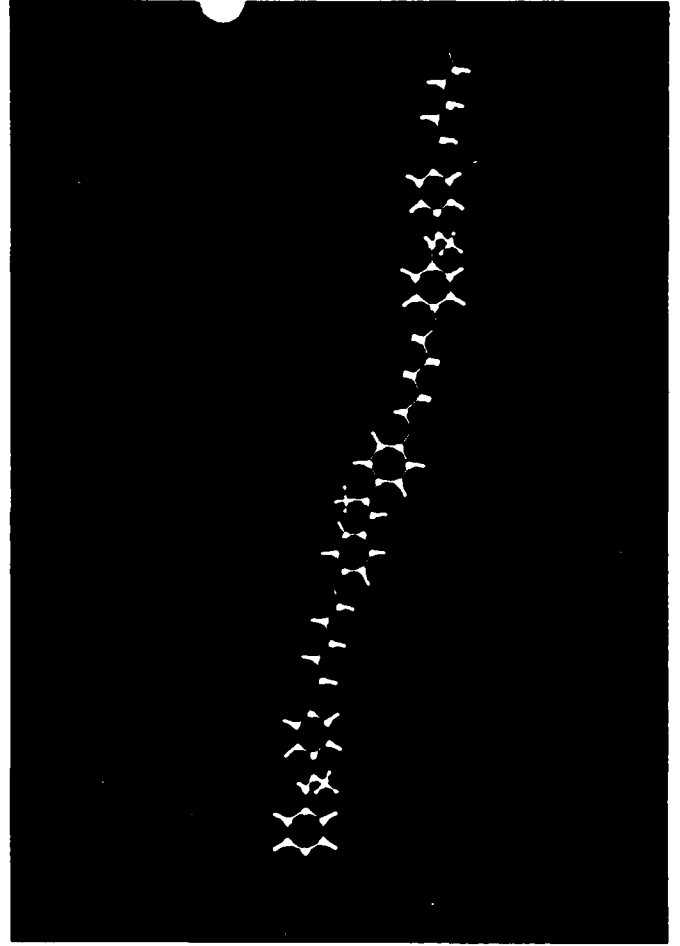
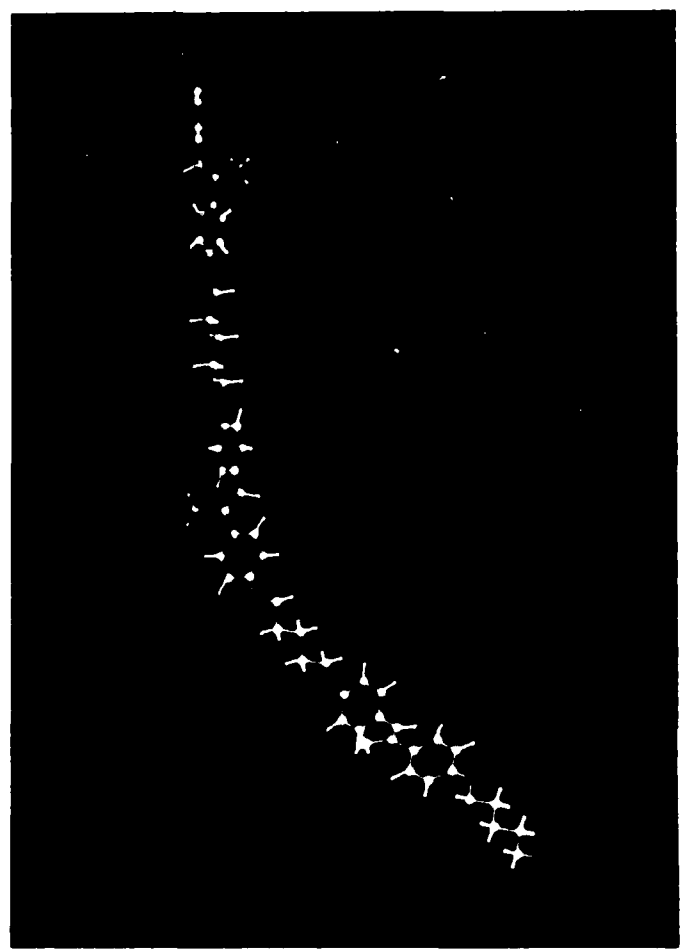
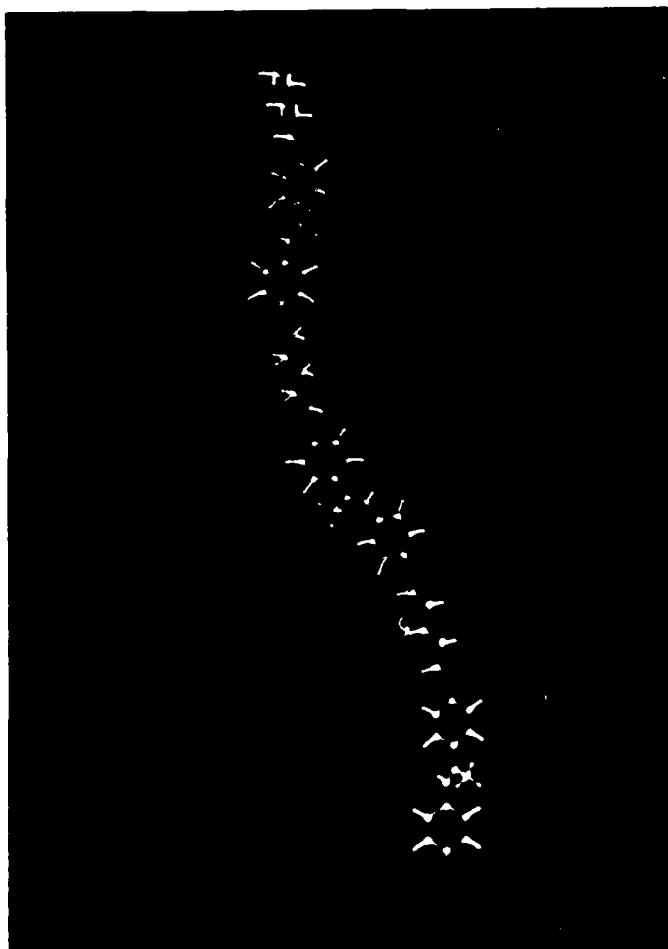


Fig. 9a



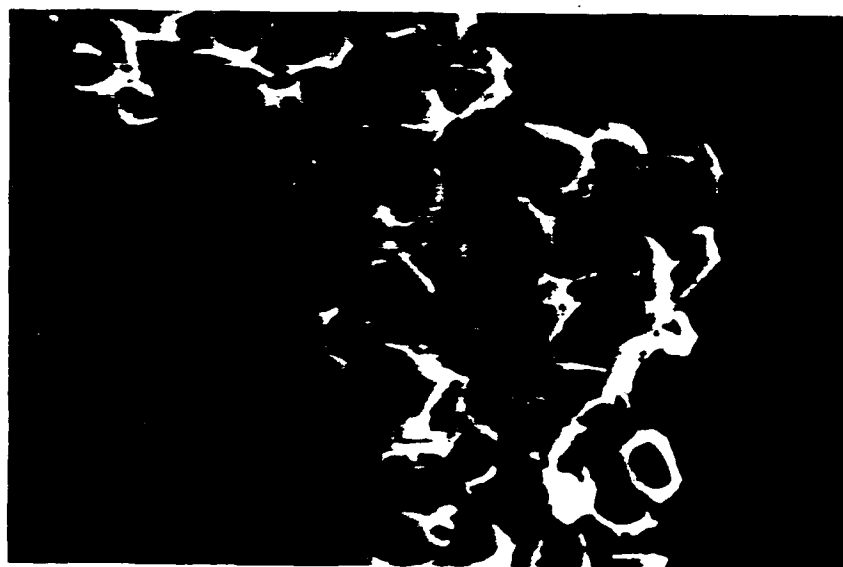


Fig. 10

1 μ m

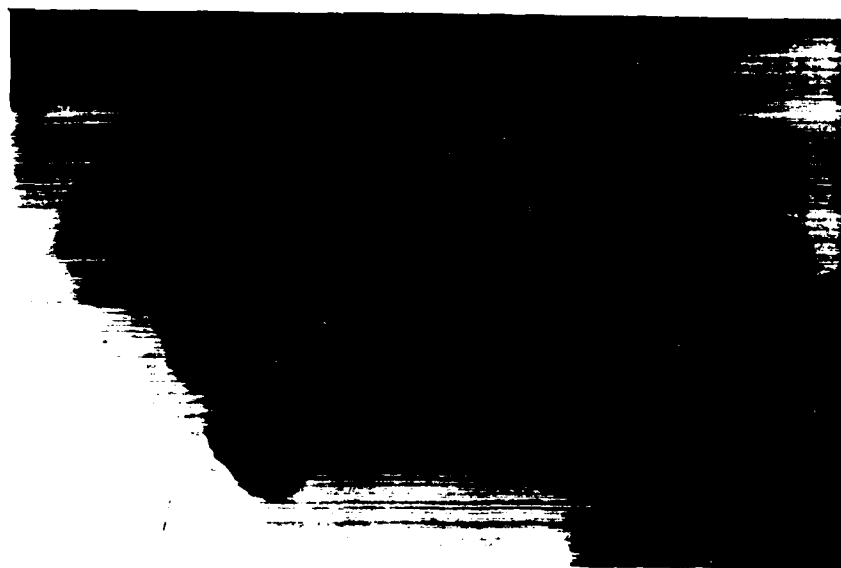
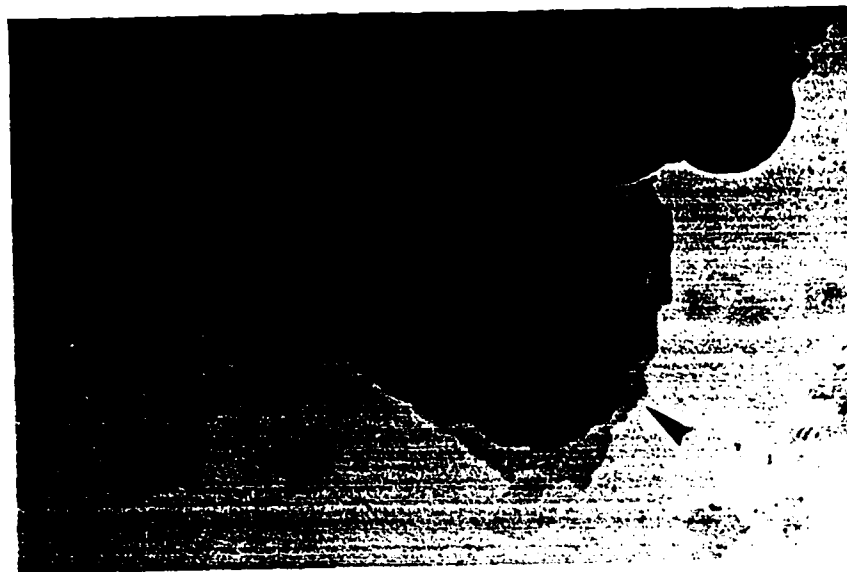


Fig. 11

1 μ m



1 μ m

Fig.12

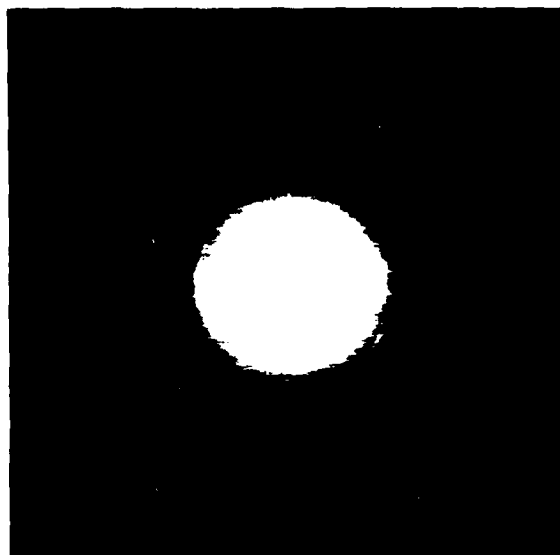


Fig.13

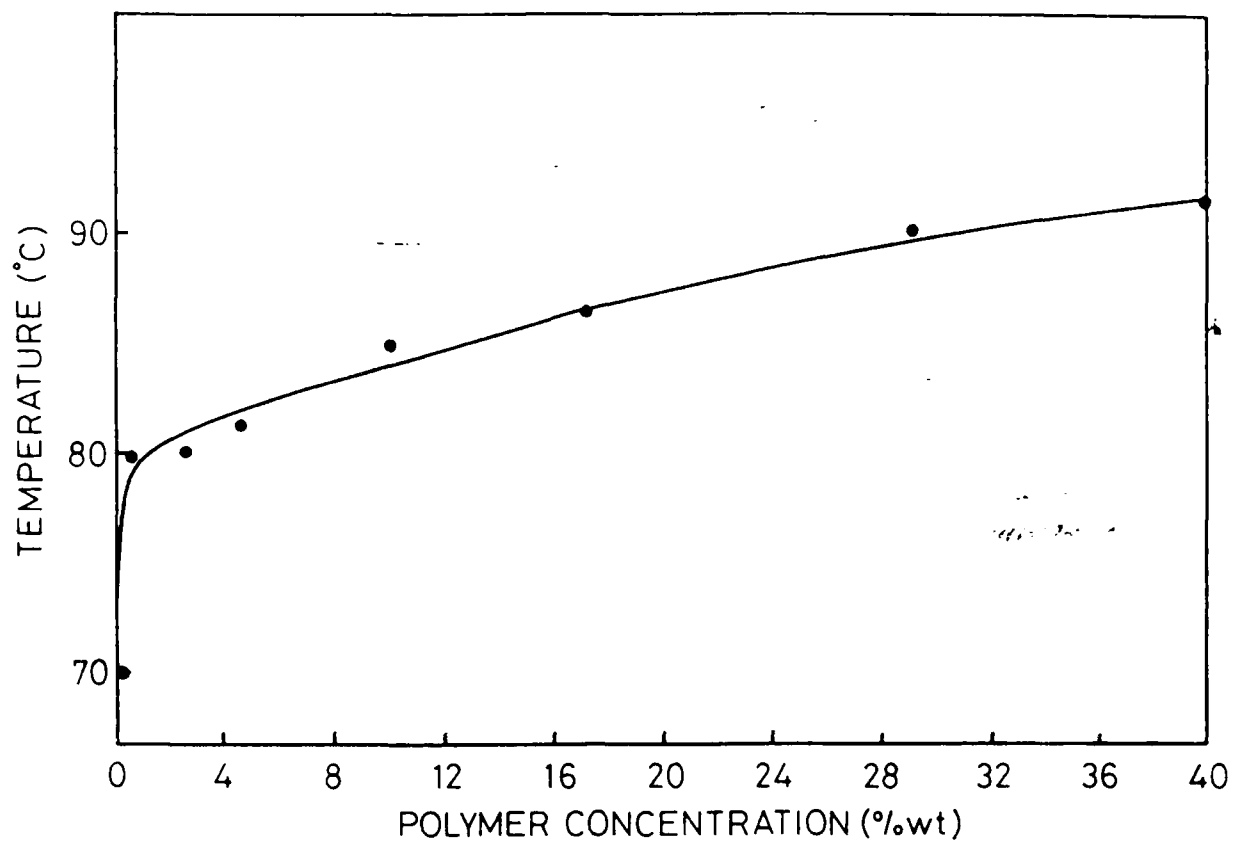


Fig.14

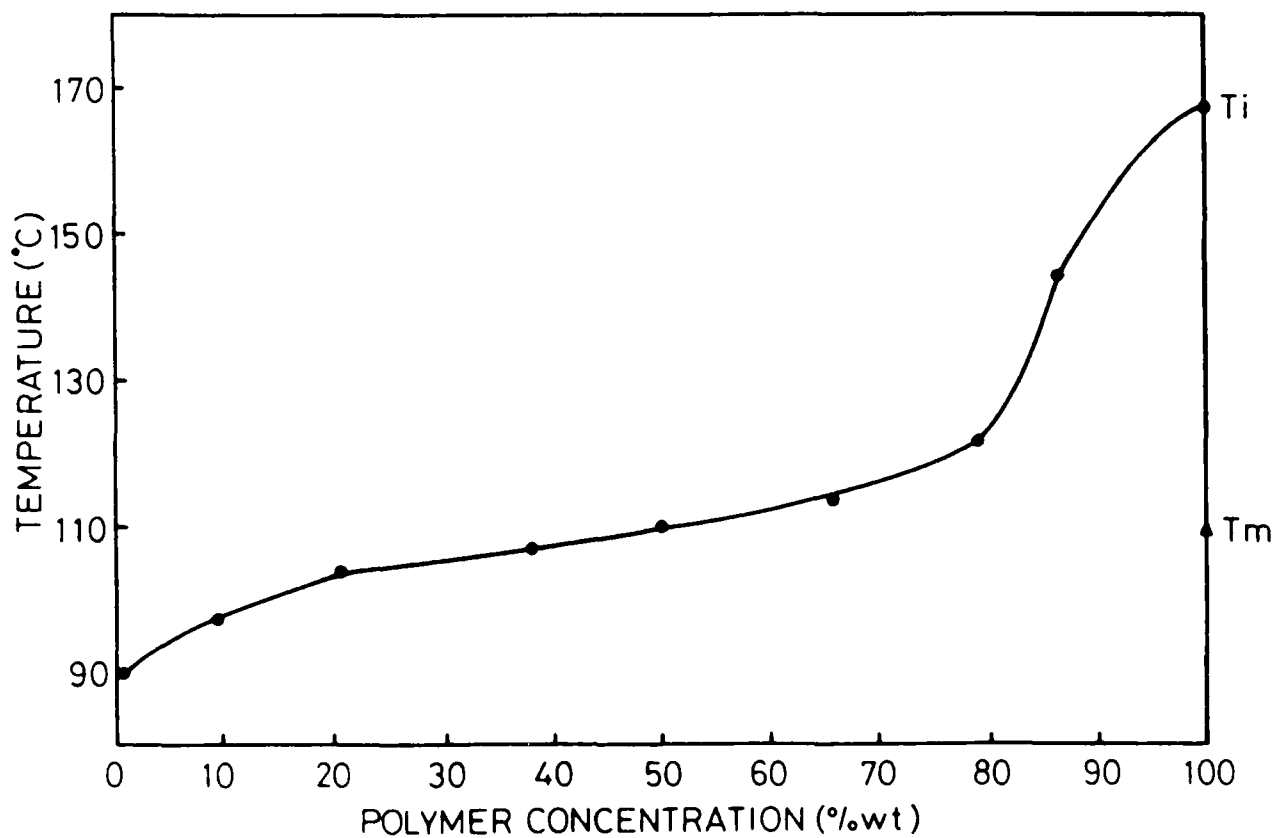


Fig.15

ENVO

DATE

FILMED

8-88

DTIC