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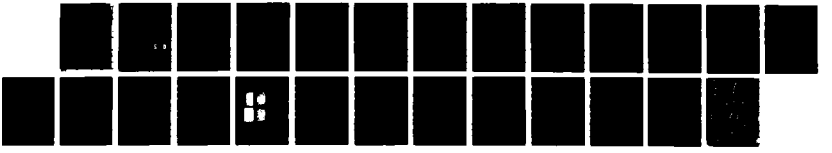

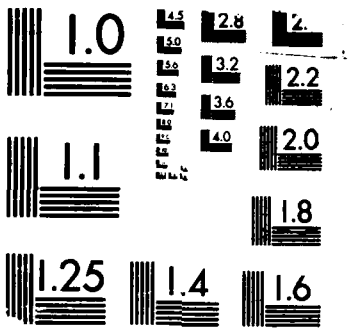

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# HIERARCHICAL STRUCTURE IN POLYMERIC SOLIDS AND ITS INFLUENCE ON PROPERTIES



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

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*4th on work performed

## SUMMARY

Work was again centred on the family of mesogen polyethers (synthetized by Professor Percec, Cleveland) serving as model substances for the exploration of polymeric structure hierarchy in polymers capable of displaying isotropic liquid crystal and crystalline phases in one and the same material.

Amongst others an unexpected feature was recognized and then explored in some depth. This is the existence of a heat treatment dependent non-equilibrium liquid crystal deficiency manifest in lowered temperatures and heats of isotropization, with parallel manifestations of an optically visible microtexture as defined by networks of disinclinations. In addition to many forward looking consequences to be exploited the above findings enabled a quantification of the 'degree of liquid crystallinity', we maintain a significant parameter for the characterization of the pertinent materials.

The previously established mesogen-spacer packing schemes have been considerably extended enabling wider generalisations to be made on the theme of the optimization of packing of molecular sequences having unequal cross-sectional areas. In the case of the present polymers this issue arises on the border line of the crystallographic and morphological but further implications are envisaged also on other levels of the structure hierarchy. As results stand they are providing significant signposts for our picture of coexistence of order and disorder. The latter are being followed up also as regards consequences for mechanical behaviour.

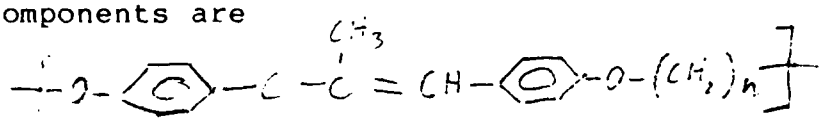
Work to establish a unified phase diagram linking the lyotropic and thermotropic states has continued and the first such phase diagram has been completed, with explicit pointers to the most profitable systems for future work on this important topic.

Work has been resumed along the previously discontinued line of orientability in the lyotropic state using the rod like PBT molecule.


## INTRODUCTION

Work during the present period was centred again on polymeric liquid crystal polyethers which have become available thanks to the cooperation of Professor V. Percec, Case Western University. These materials serve as models of main chain liquid crystal forming polymers in the service of the wider goal of exploring the full structure hierarchy in polymers capable of existing as mesomorphic and truly crystalline materials, the overall objective of our project.

More specifically, the new polyethers consist of rigid mesogen and flexible spacer sequences where the spacer length is a variable. The components are



where n is a variable (5,7,9, or 11, homopolymers or alternatively 5 and 7 or 9 and 11 copolymers). The unique advantages of these materials for our purposes, have been laid out previously.

Work during the present period continued to take advantage of these opportunities offered by the Cleveland materials. In particular, it continued the exploration of mesogen spacer packing schemes with notable further additions to our understanding. A new line of work, namely that on mechanical properties was initiated so as to explore the consequences of the newly recognized mesogen-spacer structures on mechanical behaviour. The linking of thermotropic and lyotropic behaviour was pursued further, availability of materials permitting. Most significantly and extensively, however, attention was given to a new aspect, namely to the unexpectedly arising recognition that the temperature and heat of isotropization are affected by the preceding thermal treatment of the system. This effect, as now recognized, is a reflection of the existence of variable degrees of perfection in the state of liquid crystallinity which, as it emerges, is directly manifest by light optically identifiable structure features. The largest part of the present report will be devoted to this particular topic. Finally, earlier work (Report Oct. 1985 - March 1986)on the orientability of the important rigid rod type molecule PBT has been resumed.

## I. DEGREE OF PERFECTION OF LIQUID CRYSTALLINITY AND RELATION TO MICROSTRUCTURE

It was found, while mapping the isotropic→liquid crystal phase transitions in Professor Percec's polyethers that, even when confined to the thermotropic state, the isotropization temperature ($T_i$) could not uniquely be identified just by a simple heating or cooling run in the DSC or under the optical microscope because there were variations from run to run and/or sample to sample. It was observed that, just as in the case of crystalline polymers, the value of $T_i$ is affected by the thermal history of the sample accompanied by optically visible texture changes in the microstructure characterising the liquid crystalline state. This recognition, which to our knowledge has no precedent, should have wider ranging consequences. Consequently, somewhat departing from our initial objective we set out to examine this effect more specifically. As a result, it became possible to identify and characterise quantitatively non-equilibrium liquid crystal deficiency, analogously to the familiar degree of crystallinity determinations in the crystalline state of semi crystalline polymers, and to correlate this, with the microscopically observed disinclination density, i.e. with a feature of the microstructure on the optical level of the structure hierarchy. This finding was presented at the International conference on Liquid Crystal Polymers, Bordeaux July 20-25, 1987 and submitted for publication in the Conference proceedings[1]. The material as reported below is compiled from the above text.

### Materials and Methods

The materials used in this study were main chain random copolyethers of 4,4'-Dihydroxy-α-methylstilbene (HMS) and 1:1 molar mixtures of 1,5-dibromopentane and 1,7-dibromoheptane. These were synthesised by phase transfer catalyzed polyetherification[2]. The random copolymers studied were with 1:1 mole ratio of 5 and 7 $-CH_2-$ units, and they have the general formula given in the Introduction.

A Perkin-Elmer DSC-2 calorimeter was used to measure the thermal properties of random copolymer samples as a function of temperature. Various heat treatments (annealings) were also carried out in the calorimeter when the need for these arose. The heating rates used were $10^{o}$K/min.

Solvent-cast films were prepared on microscope cover glasses and used to test specimens for optical microscopy. Isothermal heat treatment of the films was performed by placing the specimens in the D.S.C. sample holders. Selected samples were examined under the polarising microscope.

## Results and Discussion

Figure 1 displays three transition temperatures, glass transition ($T_g$), crystal melting ($T_m^{max}$) and isotropization ($T_i$) as a function of molecular weight ($\bar{M}_n$). Here $T_m^{max}$ represents the maximum melting temperature of the most stable crystal form obtainable by heat annealing at small supercoolings. As anticipated, all three transitions first increase and then level off with $\bar{M}_n$. $T_i$ the principal subject of our investigation, initially increases sharply with $\bar{M}_n$ until $\bar{M}_n \simeq 12000$. From thereon, while broadly levelling off, the data points are multivalued. It did turn out that this variability is affected by heat treatment both below and above the crystal melting point $T_m$ prior to isotropization. In view of the fact that the as-measured $T_i$ is generally thought to be an equilibrium quantity this behaviour is unexpected and was examined further.

Figure 2 shows DSC thermograms corresponding to the isotropization transition as a function of heat treatment time for $\bar{M}_n = 17700$, in this case below $T_m^{max}$. As seen, both the transition temperature $T_i$ and the heat of isotropization ($\Delta H_i$), as assessed from the endotherm peak area, are increasing with annealing time. It follows therefore that $T_i$ and $\Delta H_i$, simply as measured, may not correspond to equilibrium values beyond a certain molecular weight, $M_n^c$, and it is necessary to anneal the sample for the equilibrium to be approached. Beyond $M_n^c$, the molecular weight dependence would then reflect the lowered mobility of the chains, and in particular that of the mesogenic units.

Figure 3 displays the polarising optical images for the same samples as in Fig. 2. The dark lines, are most likely to be disinclinations circumscribing, what appears as "domains". The size of the "domains" increases with annealing time, the texture coarsening and the number of disinclinations reducing accordingly. The latter in itself would entail a reduction of net enthalpy and free enthalpy of the nematic phase thus, at least in a qualitative sense, correlating with the trend in the thermograms of Fig. 2.

The above findings allow a sample which is in an imperfect nonequilibrium state to be characterized using the measured heat and temperature of isotropization, $\Delta H_i^\infty$ and $T_i$, in relation to the corresponding equilibrium values $\Delta H_i^\infty$.

We assume an exponential approach of $\Delta H_i$ to $\Delta H_i^\infty$ and find the latter parameter by linearizing $\ell_n . (\Delta H_i^\infty - \Delta H_i(t))$ versus annealing time t (fig. 4). This then provides $\Delta H_i^\infty = 12.5$ J/g for the heat of isotropization in the equilibrium state. With this value we can then characterise a sample by considering $\Delta H_i(t)/\Delta H_i^\infty$ a quantity which, risking some objections to the term, may, in analogy with crystalline polymers, be termed degree of liquid crystallinity.

Values of $(\Delta H_i(t)/\Delta H_i^\infty).100$ together with the actual $\Delta H_i$ values as a function of annealing time are plotted in Fig. 5. As seen, the $(\Delta H_i(t)/\Delta H_i^\infty)$ 100 values range from 39% to 72% representing the perfection of liquid crystallinity as a percentage of its equilibrium value.

The reason that in the experimental series presented here the heat treatment was conducted below $T_m^{max}$ is that some oxidation of the polymer was detected during prolonged annealings in air above $T_m^{max}$. Currently, vacuum annealings are being performed above $T_m^{max}$, $T_m$ i.e. while in the nematic state. In the latter case shorter annealing times are required to obtain the same $\Delta H_i$ value than for heating below $T_m$.

The preliminary results here presented contain, in our view, an essential recognition: namely that in high molecular weight material there can exist non-equilibrium states of liquid crystallinity, where departures from the equilibrium states can be quantified calorimetrically and also correlated (even if so far only qualitatively) with the scale of the disinclincation texture as observed visually under the polarising microscope. Above all, this recognition is essential for the correct identification of isotropization temperatures ($T_i$). The observed effect also presents an opportunity for experimental determination of the free enthalpy of disinclinations. The work on this issue is currently in progress.

The above recognitions should be of consequence not only for continuing studies on these particular polymers but also for high molecular weight thermotropic polymers in wider generality. In the liquid crystalline state in particular the rheological properties, hence processability, is expected to be influenced by the perfection of liquid crystallinity as presently identified, consequently by the corresponding disinclination texture. In this context the so far unspecified "domains", currently being invoked in the field of polymeric liquid crystals to account for their rheological behaviour, would thus receive an explicit and quantitative structural meaning in mesomorphic melts thus extending the conception of structure hierarchy to the, from the processing point of view, molten state. Further, on solidification the existence of such domains are expected to carry over into the crystalline state, thus defining as yet another level of structure hierarchy within semi crystalline polymers such as have passed through a mesomorphic state.

## II MESOGEN - SPACER PACKING

### Preliminaries

The background to this subject has been extensively treated in the preceding Report (October 86 - March 87). At this place some significant additions will be reported enabling more widely ranging generalizations to be made. For self contained reading some principal statements, facts and one figure (fig. 6) will be recapitulated first.

The conclusions to be quoted are derived from X-ray diffraction patterns of oriented fibres. [These diffraction patterns (see Report Oct. 86 - March 87) reflect organizations such as span the degrees of ordering usually associated with liquid crystals and true crystals]. Such diffraction patterns serve to explore and define the organizational principles involved when packing chains which consist of mesogens and spacers of grossly differing cross-sectional areas. Two extreme packing modes have been identified referred to as "chess board" (or "Intermeshed") and "layered" packing, recapitulated by Figs 6a and 6b respectively (see also ref. 3).

The new work in this area relates to the layer packing in Fig. 6(C). As discussed previously, here the mesogen packing is optimized at the

expense of spacer packing where the much more slender spacer will not be able to pack optimally. As discussed in the preceding report one consequence of this is that spacers beyond a certain length will coil up to some extent so as to fill space better at the expense of departure from the lowest energy extended conformation. Further, due to excess space between the mesogen layers spacers of unequal lengths can also be accommodated, thus providing a pattern for the organization of copolymers. All in all, the above type of layer structure provides examples for the occurrence of alternating order and disorder in specific molècular terms which should be helpful for the visualisation of the nature of layer structures in the structure hierarchy also of explicitly crystalline polymers.

Work during the present period has examined further the mesogen-spacer organization within the "layer" category through the study of diffraction patterns such as were illustrated in the preceding report. In addition, calorimetric work was carried out in support of the conclusions and work on investigation on mechanical properties was initiated to explore the consequences of the different newly recognized schemes on the level of mesogen-spacer organization in the structure hierarchy.

## The New, Widened Organizational Scheme from X-ray Results

The previously reported scheme has been considerably extended thanks to new diffraction results, in particular on the longer 11C atom spacer, which has only been touched upon previously. The important addition here is the recognition of oblique layer surfaces as manifest by splitting of the large meridional spacings in the diffraction patterns (4 point patterns). Such obliquities have been noted before (Report March - September 1986) - but their full significance has only emerged recently, in particular that they are characteristic of the longest spacer containing system. The significant point here is that the layer periodicity corresponds to that of the extended spacer length, but this as referred to the oblique structure.

Table 1 provides a synthesis of our results in the area of mesogen-spacer packing as a function of spacer length obtained so far. It displays the overall trend and principles involved in the light of which the role of the newly reemphasized obliquity in the case of the 11C spacer will be apparent. As seen, there are 3 classes of organization:

i) extended non-crystalline spacer (2nd column)
ii) contracted non-crystalline spacer (3rd column) and
iii) extended crystalline spacer combined with tilted structure (4th column).

The sequence i)-iii) reflects increasing spacer length.

The underlying principle is based on the optimisation of the free energy for the system with unequal mesogen - spacer cross section, and is as follows. In i) (spacer length 5C atoms) the spacer is in the lowest energy conformation but with the most deficient packing. In fact the density here is lower than in truly random amorphous material; thus in spite of the parallel chain arrangement the spacer system remains non-crystalline. Here it is the gain in free energy due to the most favourable chain conformation which dominates the organizational behaviour, because coiling up, even with consequent improvement of packing, in the case of such a short chain length does not lead to

sufficient entropy gain to lower the overall free energy below that of the loosely stacked parallel chain arrangement.

In ii) the spacers are long enough to coil up and thus improve packing at the expense of the lower energy extended chain arrangement. Here clearly the higher conformational entropy combined with denser packing leads to overall lowering of the free energy, thus resulting into what can be considered as an approximation to a truly random amorphous structure. The copolymer 5,7 case is clearly a mixture of i) and ii), spacer 5 behaving as in i) and spacer 7 as in ii) in one and the same, stack of layers.

In iii) with tilted mesogen layer interfaces the spacers can come closer together laterally. This will improve packing so as to make the overall extended arrangement again viable in cases of such still longer spacers, where there is sufficient chain - chain interaction in the extended form to make such an arrangement energetically stable.

We thus see that increasing of spacer length leads to a sequence of extended → random → extended (with tilt) spacer chains, a structure principle we believe of general applicability.

The closer spacer packing in case iii) coupled with the extended configuration implies that some kind of crystallization is involved for spacers long enough to do so, in spite of their attachment to the mesogen. It is this latter point we set out to test by the calorimetric work to follow.

## Heat of Fusion

The molar heats of fusion ($\Delta h_f$) were determined for the different layered structures as a function of spacer lengths. Results are shown by Fig. 7. We see that $(\Delta h)_f$ is a constant for up to spacer lengths of 9. We interpret this value of 11 KJ/mol as due to the mesogens which, as we know from X-ray diffraction, form closely packed layers. The value for the 11 spacer, however, is twice as large (22 KJ/mol). We attribute this excess in $(\Delta h)_f$ to some form of crystalline order within the spacer layer. The corresponding additional heat of fusion, 11KJ/mol, however, is considerably lower than that of the fully crystalline alkane of corresponding length in its stablest o-rhombic form. It is even less than the enthalpy of the "rotator" phase of n-alkane C11H24 which is 22KJ/mol, nevertheless sufficiently high to attribute it significance in terms of packing of alkyl chains. The results therefore suggest that the alkyl spacer layers in PHMS-11 are themselves in a mesomorphic state of order between those of the rotator phase and the melt. This state of order could be similar to that found in the so called "gel phase" in lipids. The latter arises from parallel but loosely packed alkyl chains which are "tails" attached to much larger hydrophilic "heads", hence involve the same organizational issue, namely optimization of overall packing in chain type molecules consisting of portions with differing cross-sectional areas.

We thus see how the present study of chain packing, as affected by mesogen - spacer ratio, is leading us to general schemes resting on basic principles and tying up with other aspects of molecular science. At this stage we may venture some predictions. Namely, when increasing the spacer lengths still further we would expect the spacer packing to improve further while still in the extended form, ultimately leading to a spacer layer where the alkane chain portions can be fully crystalline as in a paraffin. This should have further interesting consequences,on

the theme of hierarchical structures in high polymers. New material for such a thrust are being awaited. In the meantime we have turned to explore possible consequences for macrosocopic behaviour of samples we already possess to be briefly outlined.

## Mechanical Measurements on PHMS-7

Mechanical measurements were performed on PHMS-7. the primary aim of these measurements was to compare the macroscopic mechanical behaviour of the "chessboard" and the "layered" crystal forms. It was anticipated that this would reflect the two different modes of coupling of hard (mesogen) and soft (spacer) molecular segments in Fig. 6(B and C respectively), i.e. parallel coupling in the "intermeshed" (chessboard) and series coupling in the "layered" form.

Dynamic mechanical measurements were carried out on thin fibres using the vibrating reed method, as this was most suitable for the small amount of material available. The temperature range between 23 and 100 deg.C was covered and the structures achieved were verified by X-rays on identically treated fibres. The maximum accessible frequency range was beteeen 20 Hz and 2kHz. The apparatus used was designed by Dr. R. Arridge of Bristol Physics Department. (For method see Appendix).

Figure 8 shows the frequency dependence of longitudinal Young's modulus of PHMS-7 fibre (7 carbon atoms in spacer) in the "intermeshed" crystal form at different temperatures. The steep decrease in modulus with increasing temperature between 23 and 50 deg. C is the result of the glass transition. The loss factor shows a pronounced maximum in the same $T_g$ temperature range, thus paralleling the trend in modulus (Fig. 9).

Results of the above kind are available so far only for the "intermeshed" structure. Even at this stage the magnitude of the effect of the glass transition is surprising given the fact that the amorphous fraction in the sample is so low that $T_g$ could barely be detected in the corresponding thermograms (report March-September 1986). While it is of interest in itself of how a minority fraction of uncrystallized material is related to the structure hierarchy to have such a dominant effect, it poses questions as regards the foreseeable mechanical distinction between the two structures in Figs 6. In view of this, other ways for showing up the differences in molecular stress distributions in the two types of specimens are being currently thought of before extending the above type rather labour intensive measurements to the "layered" structures. In the meantime useful insight in the mechanical behaviour of this class of material has been gained, together with experience in such mechanical experimentation.

## X-ray and Mechanical Information in Aid of Interpreting DSC Thermograms

At this point it is instructive to illustrate a DSC thermogram on a sample of PHMS-7 of low crystallinity displaying pronounced $T_g$ effects which, as will be seen, is in good agreement with the mechanically determined $T_g$. Fig. 10 shows the DSC thermogram of such a melt-quenched PHMS-7. the following features are observed: 1) a step increase in heat capacity centered around 20°C - this is associated with $T_g$: 2) an exotherm starting around 30°C, associated with cold crystallization of the A form; 3) another exotherm starting at around

100°C, associated with the A→B (see Appendix) crystal transition; 4) an endotherm at about 130°C attributed to melting of the "intermeshed" form (form B); this is followed by yet another exotherm and a sharp endotherm at 145°C, ascribed to recrystallization and melting, respectively, of form C ("layered" form). This example illustrates how the complex DSC thermograms of liquid crystal forming polymers can now be explained with fair certainty as a result of the parallel X-ray and mechanical studies of their polymorphic and thermotropic behaviour. Conversely, it is worth reflecting upon the limitations of DSC thermograms on their own, the main guides used in liquid crystal polymer studies in general, without the backing of other sources of information such as we are currently bringing to bear on the subject.

## Wider Implications of the Issue of Mesogen-Spacer packing

At this point it is opportune to refer to the wider perspectives arising through the present studies on mesogen spacer relation. Packing problems created by unequal cross-sections of consecutive entities is a central theme in polymer structure science. It is not generally recognized that this same underlying theme emerges in different forms throughout all the dimensional levels of the structure hierarchy. When it arises,say, as a result of aliphatic-aromatic sequences in a conventional terephthalic acid based polyester it becomes an issue of molecular packing in the otherwise perfect crystal structure (see ref. 5). When the same issue arises in the case of a mesogen-spacer sequence on an only slightly larger dimensional level then it becomes a controlling factor in liquid crystallinity, incomplete crystallinity, rotator phases, defect layers etc. as in the present polyethers. As already mentioned, the same issue is at the basis of the structure of lipids, membranes etc. of immense biological significance. On a still larger (hundreds of A) scale the same factors are at play when considering polymer crystal lamellae with chain folded surfaces, and in fact underly the whole subject of alternation of amorphous and crystalline zones, a basic feature of semi crystalline polymers, specifically the amount and nature of molecular continuity, when a chin passes through high and low density regions consecutively. And the theme can be taken further up the size scale, to dimensional changes in localized yielding (crazing, micronecking etc.). If the purely geometric issues are widespread and profound so are even more the potential consequences for mechanical behaviour (uneven load bearing, parallel v. series coupling etc.) an area we have just started to explore from the present viewpoint, and which again encompasses the full dimensional hierarchy from the molecular (in the crystallographic sense) to the macroscopic. In all this dimensional range the mesogen-spacer level is at the crucial junction of what is normally regarded as crystallographic and morphological.

## III. COMBINED LYOTROPIC-THERMOTROPIC PHASE DIAGRAM

A further step was made towards the establishment of a combined lyotropic - thermotropic phase diagram, one of the main steps towards the unification of two hitherto separate areas of lyotropic and thermotropic materials, an opportunity presented by the new polyethers. The work was limited (due to limited amount of material - further dispatches from Cleveland are expected), yet we think significant, as it has led to the completion of the first such phase diagram, shown by Fig. 11. The addition since the last report (Sept. 1986 - March 1987) is the essential distinction between liquid crystal and true crystal carried out by DSC (in addition to the light optical determination of

the isotropy-anisotropy boundary). Compared to a priori expectations the liquid crystal regime is at the high concentration end of the phase diagram and the concentrated side of the expected "chimney" merges with the thermotropic ordinate and is thus not discernible. Nevertheless, it is clear that this is due to the corresponding high flexibility of PHMS-5/7. By theoretical expectations (6) a more rigid molecule, hence one with shorter spacer, would narrow the biphasic gap and shift it to lower concentrations. This would make the "chimney" apparent and prominent as bending over and linking up with the thermotropic ordinate as predicted (see report April-September 1986) but not reached so far. The same trend would be promoted also by the suppression of crystallisation which would bring the liquid crystal regime more in prominence. This would arise e.g. if the mesogens where suitably altered. New materials in service of this enquiry are being expected from Professor Percec, Cleveland.

## IV ORIENTABILITY OF RIGID ROD MOLECULE - PBT

Towards the end of the present period we have resumed work on the orientability of PBT (poly p-phenylbenzthiozole) in solution and lyotropic state as commenced during an earlier period (Report September 1985-March 1986) but not pursued further at the time. This is both a structural material important in its own right and also serves as a model for the idealised rod shape rigid molecule. Here this initiative is merely being announced, results will be reported next time. This work is drawing also on other resources and long standing experience of the laboratory, which in the past has centered on Dr. J. A. Odell who continues to be associated with it.

## RESEARCH PLANS

The results of the present and preceeding periods have revealed wide ranging opportunities along a broad front. Even if individually some of the items may appear disconnected they are different aspects of the same overriding themes: hierarchical structure and orientibility. Planning at this stage means choosing between the numerous opportunities. Such choices are influenced by three factors: intrinsic significance, practicality and availibility of materials. Except for PBT, in the latter respect we are relying on Prof. Percec's synthesis and delivery which, as before, is to provide us with new opportunities but at the same time remains a determining factor in our choices. Within these limits the future plans will embrace the following items.

Mesogen-spacer stacking. The newly arrived at scheme (Table 1) will be pursued extending it to other spacer lengths. As enunciated previously, this is to test the schemes' limits of validity in terms of mesogen-spacer ratio, including at one end of the spectrum the linking up of this family of materials with those containing no spacers at all and in the other extreme, with materials where the spacer is the dominant constituent approaching the behaviour of the pure alkane chain. Beyond the above, it is proposed to establish the link up between crystal structure, mesomorphic behaviour and higher level hierarchy based on the theme of uneven cross-section of chain constituents. In this we shall draw on a wide range of polymeric materials, even beyond those of Prof. Percec's, containing both aromatic and aliphatic constituents. It is planned to explore the consequences of all the above coupling and packing modes in terms of stress response.

Perfection of liquid crystallinity. The new recognition that there exist such features as non-equibilbrium 'degree of liquid crystallinity' and that this has visible manifestations in texture will be pursued. In particular, the deficiency in liquid crystallinity is to be accounted for in terms of disclination density as identified microscopically. Further, the effect of the textures (thus defined by the disclinations within the liquid crystalline state) on the crystalline structure hierarchy following crystallisation will be explored. If found practicable at this stage, establishment of a connection between the newly recognised 'degree of liquid crystallinity' and flow behaviour in the mesomorphic state will be attempted.

Unified lyotropic-thermotropic phase diagrams. The importance of exploring this possibility with the Cleveland polyethers will be pursued along lines outlined in the preceeding report together with its numerous potential consequences there indicated. The latter will include the exploitation of the gel state and the many pointers for processing. As before, this item remains central from the point of view of thermodynamic behaviour and for resulting structure hierarchies. The precise path taken will depend on componds forthcoming.

Orientation. The originally proposed programme will be vigoursly pursued, in the first instance through the currently ongoing works using the rigid rod model substance PBT. Particular aspects will be; influence of flow orientation on the isotropic-lyotropic transition, and influence of external stress on chain conformation and chain packing.

## APPENDIX (On Mechanical Measurements)

The fibre of PHMS-7 was prepared by first drawing the molten nematic polymer and quenching the preoriented fibre at room temperature, i.e. just below the glass transition temperature $T_g$. The fibre was subsequently drawn at ca. 40 deg. C whereby stress-induced crystallization took place resulting in a well oriented fibre of crystal form A. (Poorly ordered layered structure defined in preceding report). The product was then subjected to annealing in a precision thermostat at 115 deg. C, i.e. above the transition point between forms A and B (form B is the "intermeshed" or chess board form, Fig. 6a, but below the B-C transition temperature (C is the "layered" form). X-ray diffraction patterns were recorded from identically treated fibres.

Fibre samples of uniform circular cross-section were subjected to forced vibrations of continuously varying frequency and the resonant amplitudes were measured opto-electrically. Resonant peak widths were also measured, from which the loss factor was determined as

$$\tan \delta = (f_1 - f_2)/f_p$$

$f_1$ and $f_2$ are the half-power frequencies, measured at amplitude values of $A_p/\sqrt{2}$, where $A_p$ is the peak amplitude at frequency $f_p$. The Young's modulus $E_i$ is obtained by the relation:

$$E_i = \frac{\rho \omega^2 \ell^4}{k^2 (m\ell)_i^4}$$

where $\rho$ is the density, w the angular peak frequency, $\omega$ the angular peak frequency ($= 2\pi f_p$), l the fibre length, k the radius of gyration (for circular cross-section of diameter d, $k^2 = d^2/16$) and $(ml)_i$ are characteristic constants for each resonance order i (for details we refer to book by Arridge[4]).

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## FIGURE CAPTIONS

Figure 1. Transition temperatures of PHHS - 5/7 (50:50) copolymer as a function of molecular weight as determined by DSC: $T_g$ = glass transition temperature; $T_m^{max}$ = maximum melting point of the most stable crystal form, achieved by annealing at low supercooling; $T_i$ = nematic-isotropic transition temperature ($\phi$ = some as-prepared samples which were transformed into the corresponding samples $\blacklozenge$ on heat treatment).

Figure 2. DSC thermograms of PHMS-5/7 (50:50), $\bar{M}_n$ = 17700. Samples annealed at 100°C: A(2.0h), B(6.4h), C(13.5h), and D(16.6h).

Figure 3. Sequence of optical micrographs for PHMS 5/7 (50:50), $\bar{M}_n$ = 17700, taken at different time intervals during annealing at 100°C. A (Unannealed), B (6.4h), C(13.5h) and D(16.6h).

Figure 4. $\ell_n(\Delta H_i^{\infty} - \Delta H_i(t))$ vs annealing time as derived from the thermograms of PHMS - 5/7 (50:50) ($\bar{M}_n$ = 17700), with $\Delta H_i^{\infty}$ = 12.5 J/g.

Figure 5. $\Delta H_i$ and $\Delta H_i(t)/\Delta H_i^{\infty}$ vs annealing time as derived from the thermograms of PHMS-5/7 (50:50) samples ($\bar{M}_n$ = 17700).

Figure 6. Schematic representation of molecular packing in forms B("intermeshed") and C ("layered"). Mesogen units are represented by rectangles.

Figure 7. Molar heat of fusion ("layered" crystal form nematic transition) for a series of well annealed PHMS-n homopolymers with increasing number of carbon atoms in the spacer (n). The constant $\Delta H_f$ for n = 5, 7 and 9 indicates that spacers do not contribute to the crystallization enthalpy. The anomalously high $\Delta H_f$ for PHMS-11, on the other hand, suggests that the $(CH_2)_n$ spacers do crystallize to some extent.

Figure 8. Frequency dependence of longitudinal Young's modulus of PHMS-7 fibre in the "intermeshed" crystal form at different temperatures.

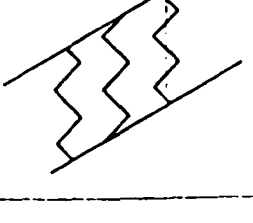
Figure 9. Temperature dependence of the loss factor (tan $\delta$) for the PHMS-7 fibre in the "intermeshed" crystal form. The values refer to the frequency of 80 Hz and were obtained by linear interpolation of the values measured at the nearest resonant frequencies. The maximum around 40°C indicates the glass transition.

Figure 10. DSC thermogram of melt-quenched PHMS-7. The different features are described in the text.

Figure 11. Phase diagram showing the isotropic-anisotropic coexistence curves in the system PHMS-517 (50:50), $\bar{M}_n$ = 12800, and Diethylphthalate. (▲) from DSC thermograms, (●) from optical microscopy using polarized light.

TABLE 1.

Three options for minimizing spacer free energy realized in layer structures of PHMS

| Spacer length ($CH_2$-groups) | SPACER EXTENDED, NON-CRYSTALLINE:<br>+ low intramolecular (conformational) energy<br>- lowest density | SPACER CONTRACTED, NON-CRYSTALLINE:<br>+ higher density<br>+ higher conformational entropy<br>- higher intramolecular energy | SPACER EXTENDED AND TILTED, CRYSTALLINE:<br>+ highest density<br>- best mesogen packing possibly sacrificed and/or Ar-O-CH bond angle strained |
|---|---|---|---|
| |  |  |  |
| 5 | o | | |
| 5,7 | | o | |
| 7 | | o | |
| 9 | | o | |
| 11 | | | o |

(+ an - signs indicate favourable and unfavourable points for the overall free energy which the system will optimise for each spacer length.)

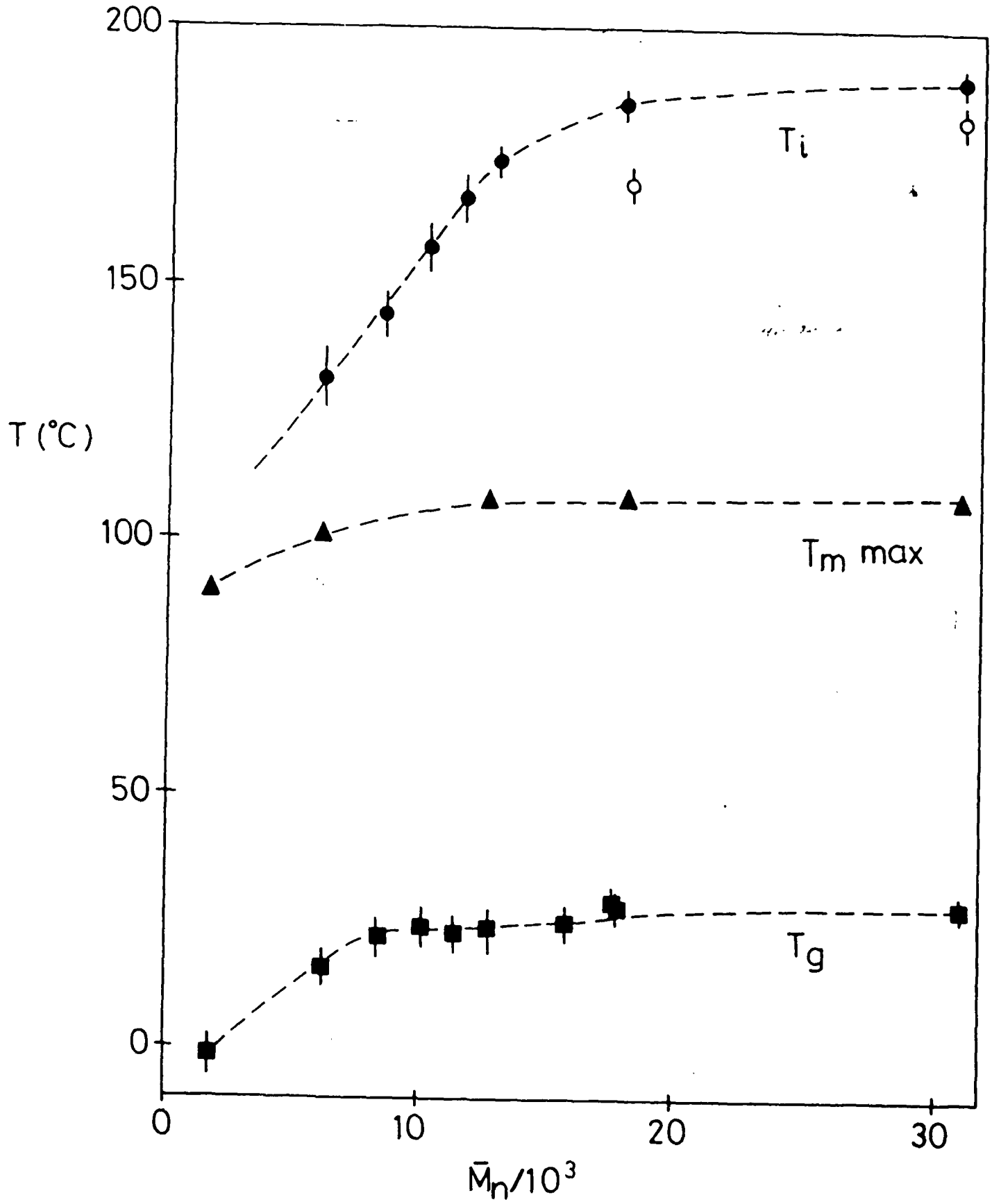



FIGURE 1.

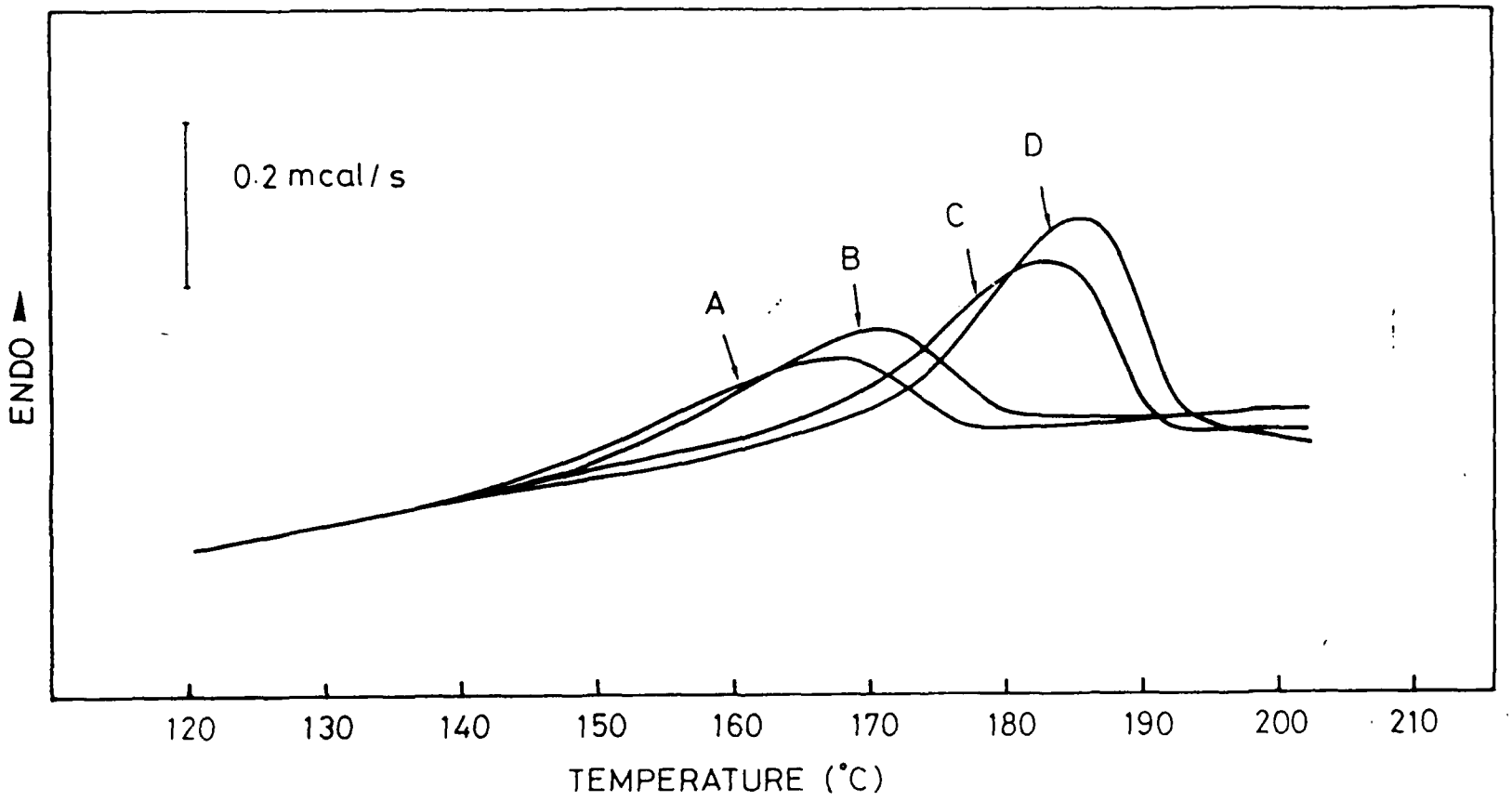

0.2 mcal / s
ENDO
A
B
C
D
120
130
140
150
160
170
180
190
200
210
TEMPERATURE (°C)

FIGURE 2.

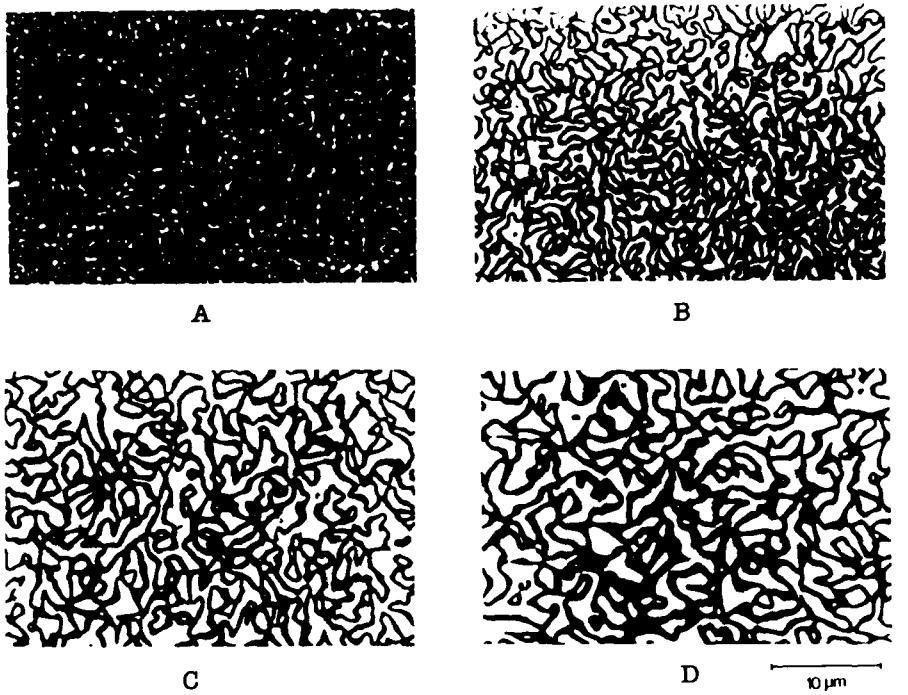



FIGURE 3.

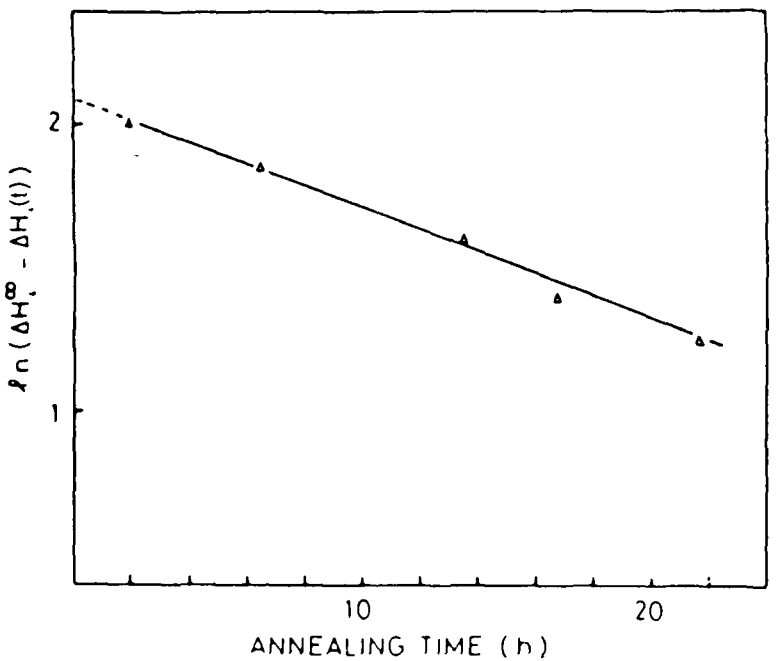



FIGURE 4.

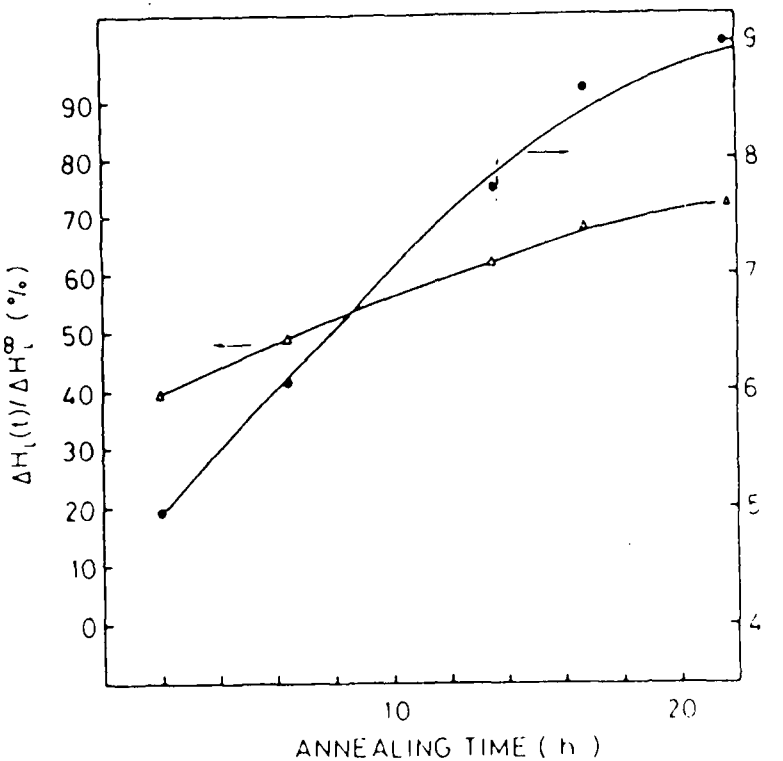



FIGURE 5.

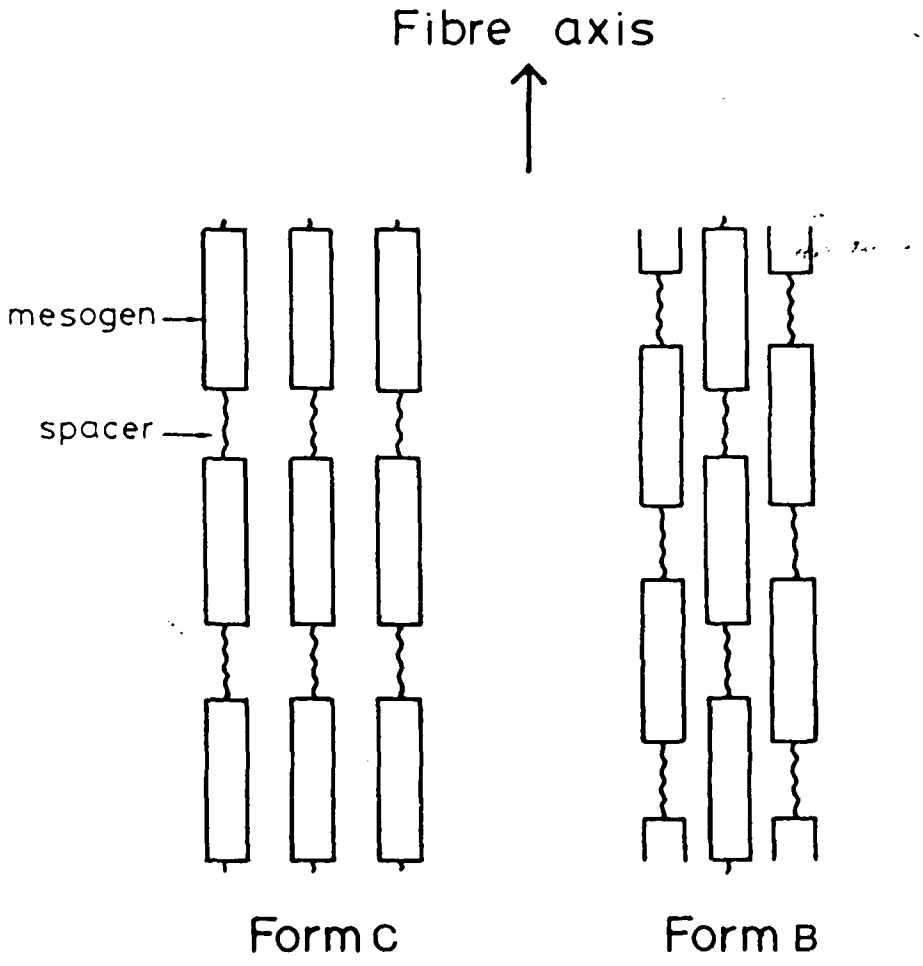



FIGURE 6.

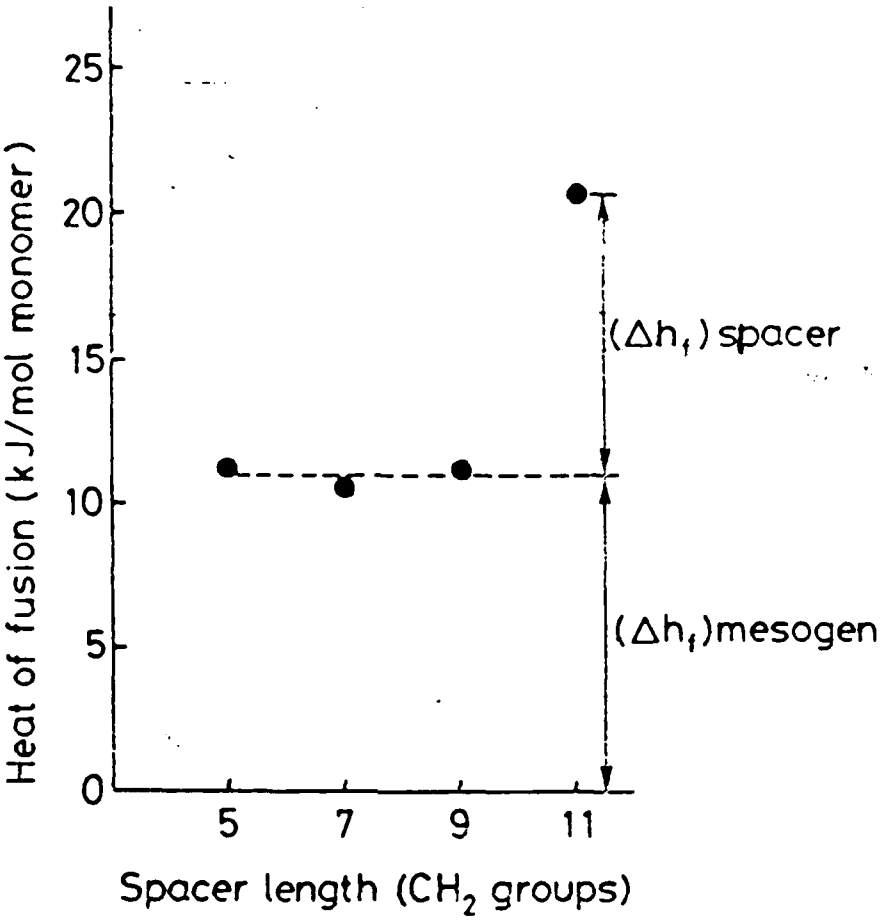

25
20
15
10
5
0
Heat of fusion (kJ/mol monomer)
(Δh_f) spacer
(Δh_f) mesogen
5
7
9
11
Spacer length (CH2 groups)

FIGURE 7.

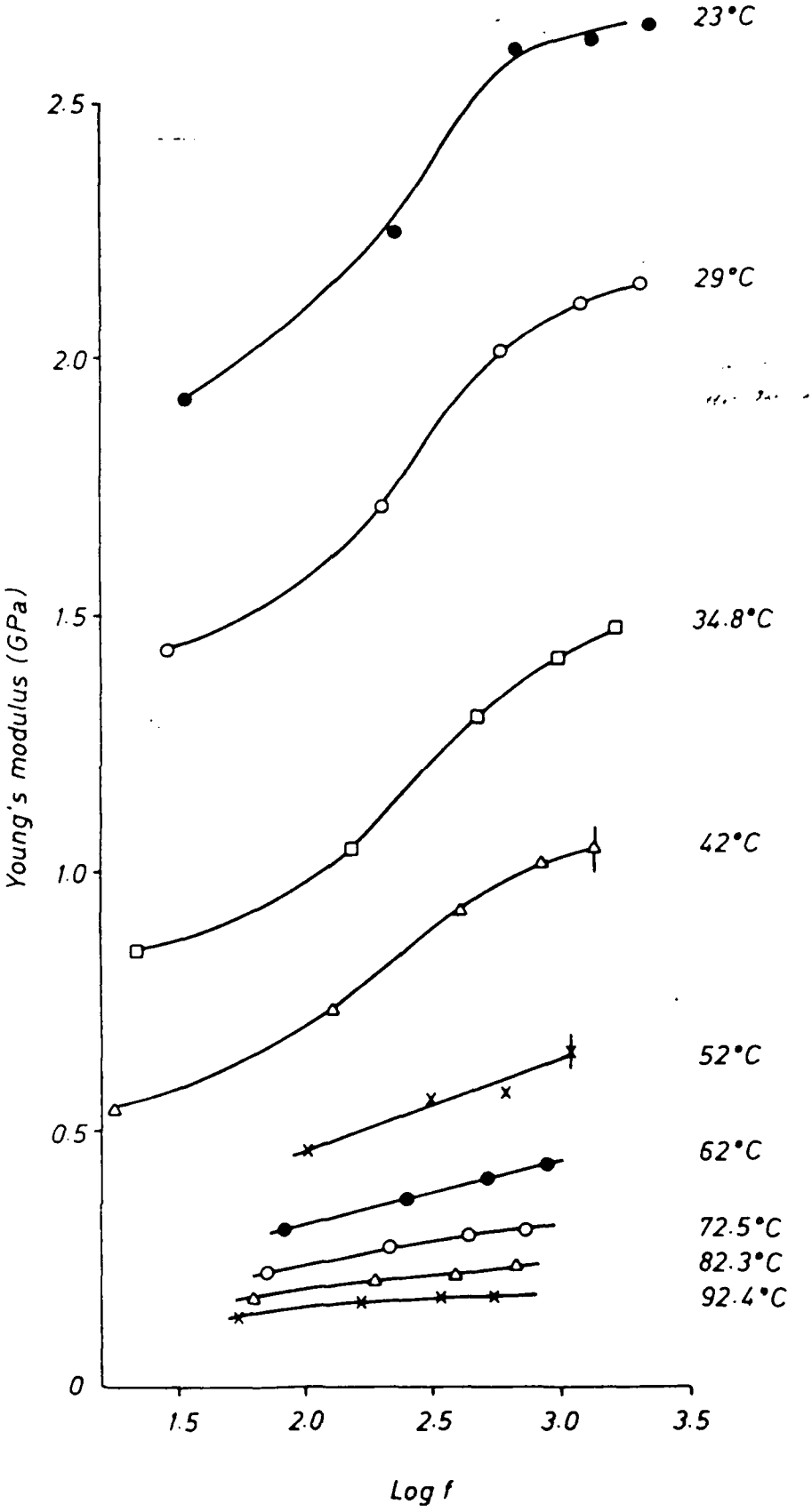

23°C
29°C
34.8°C
42°C
52°C
62°C
72.5°C
82.3°C
92.4°C
2.5
2.0
1.5
1.0
0.5
0
Young's modulus (GPa)
1.5
2.0
2.5
3.0
3.5
Log f

FIGURE 8.

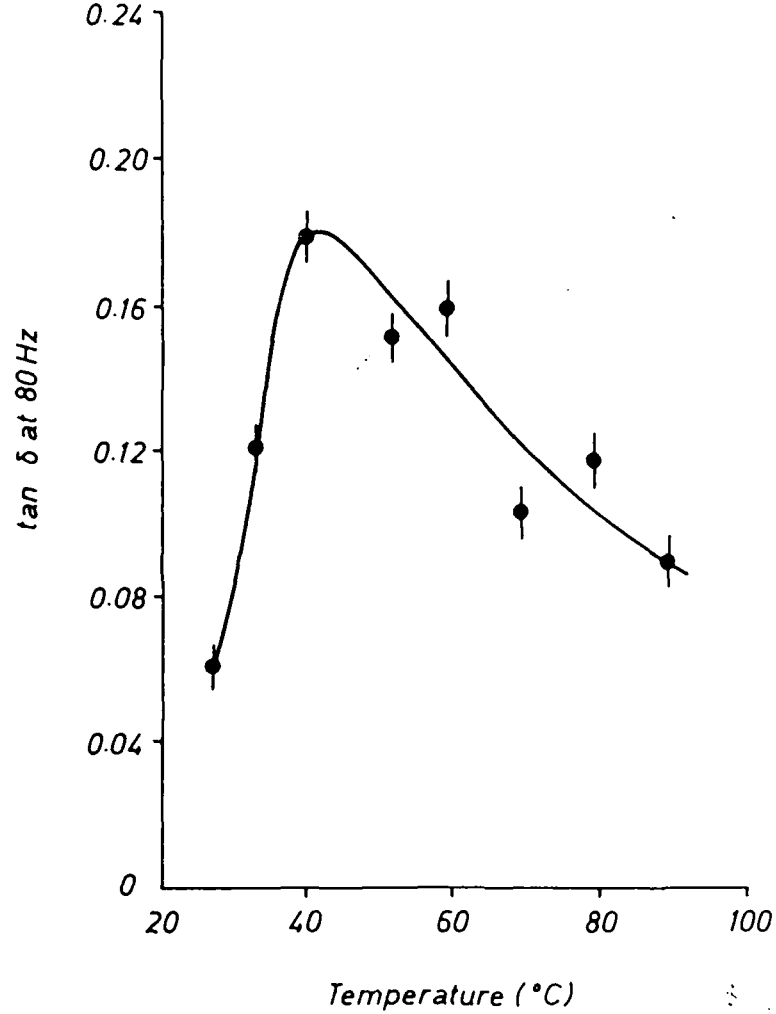

0.24
0.20
0.16
0.12
0.08
0.04
0
tan δ at 80 Hz
20
40
60
80
100
Temperature (°C)

FIGURE 9.

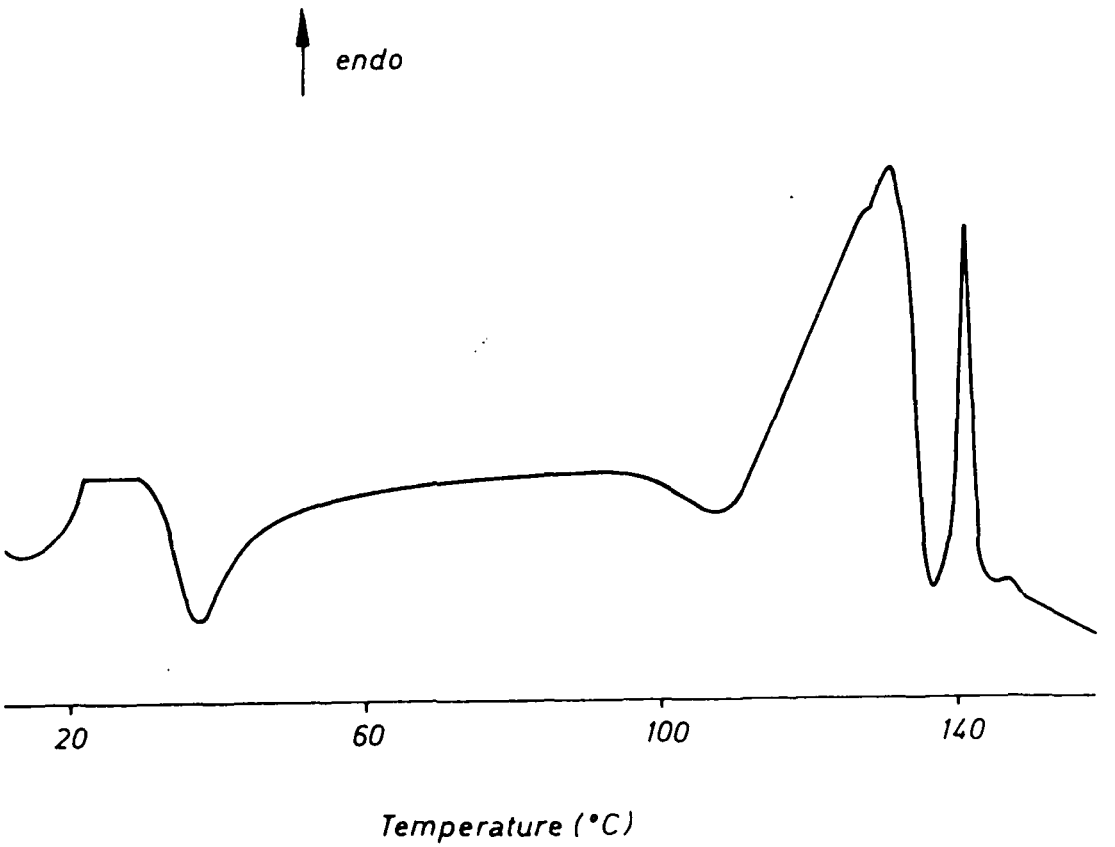



FIGURE 10.

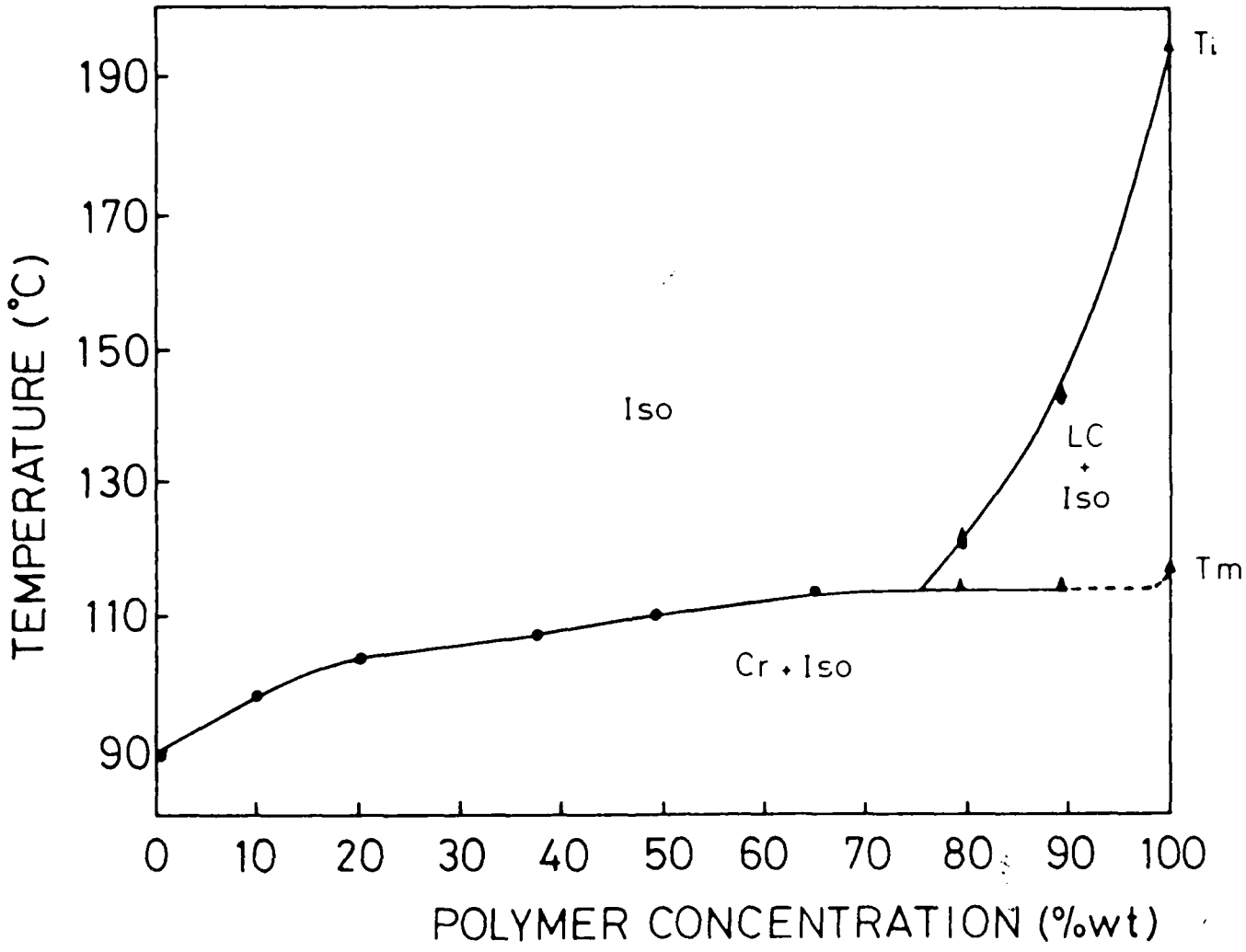

TEMPERATURE (°C)
190
170
150
130
110
90
0
10
20
30
40
50
60
70
80
90
100
POLYMER CONCENTRATION (%wt)
Iso
LC
+
Iso
Cr + Iso
Ti
Tm

FIGURE 11.

END

DATE

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