The nature of crystallites in solidified, rigid-chain, liquid crystal polymers

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(*Received* 8 *May* 1981)

Two rigid chain thermotropic liquid crystal polyesters have been examined by X-ray diffraction and thermal analysis in order to explore the nature of the crystallites in the solid state. A comparison of quenched and slow-cooled specimens indicates the presence in the quenched material of microcrystals that are too small to give clear X-ray lines. It is proposed that this is due to the very low surface energy associated with the nematic chain morphology. Both the enthalpy and entropy of fusion are much lower than in conventional polymers and are related to the molecular design of the thermotropic polymers.

Keywords Polymers; liquid; crystal; crystallite; rigid-chain; solidified

INTRODUCTION

This paper is concerned with the nature of the crystallites that form on cooling rigid chain liquid crystal polymers from the mesophase melt to the solid state. Such systems are often termed thermotropic in that the phase transitions are brought about by the variation of temperature alone, as distinct from lyotropic systems such as 'Kevlar' where the transition depends on the concentration of a solvent. The mesophase of rigid chain liquid crystal polymers is believed to be nematic; i.e., the director of the molecular units tends to a local parallel arrangement. Since the molecular units are linked into continuous polymer chains, this is tantamount to saying that the chains form near-parallel configurations in the molten mesophase. This is confirmed by the structure of extruded filaments, where the elongational flow fields readily impose a very high orientation in the melt, which on subsequent cooling to a solid gives rise to fibre-like X-ray patterns.

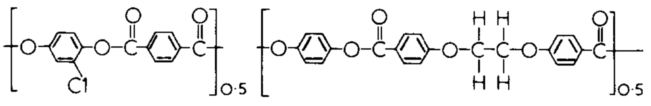
Many of the rigid chain thermotropic polymers that have been synthesized can exhibit sharp X-ray diffraction lines that can be associated with crystallites with three dimensional order. Such materials show two recognisable transitions; a T_g type of process usually at about 100°C and a crystalline melting process T_m usually over 200°C. The T_g process is accompanied by a change from a very rigid solid to a more flexible solid, while the T_m is associated with a change to a birefringent mesophasic melt of very low viscosity. The attainment of a rigid state in the interval between T_g and T_m can be attributed to the presence of the crystallites linking together the rigid chains. In this sense, the crystals form an exactly analogous function to those in conventional crystalline polymers (e.g., polyethylene at room temperature). However, when it comes to the detailed nature of the crystals, we believe there are important distinctions and the purpose of this paper is to focus on these differences. The work described is concerned with two aromatic polyesters which are typical of the rigid chain nematic polymers that are described in the patent literature. This study is not concerned with the exact crystal structures of these specific polymers but only with the more general features that are common to all of this type of liquid crystal polymer.

EXPERIMENTAL

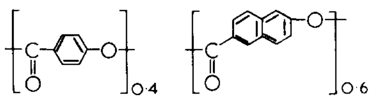
Samples

The two liquid crystal polyesters that have been examined were synthesized according to the methods described in the respective patent literature and had the following nominal compositions:

Polymer A[1]



Polymer B[2]



The segments are believed to be randomly linked. Solution viscosity behaviour suggests the molecular weights of the polymers are in the range 10 000 to 30 000.

It is clear by inspection that polymer **B** has a stiffer chain than polymer A and that both are in turn stiffer than polyethylene terephthalate (PET) which is a well known conventional polyester.

Thermal analysis

10 mg samples were weighed into d.s.c. pans and were scanned in a Perkin Elmer DSC2 at 40°C min^{-1}. The instrument was linked on-line to a computer that allowed the output to be corrected for baseline curvature and to be calibrated in absolute units.

For polymer A, two sets of specimens were prepared.

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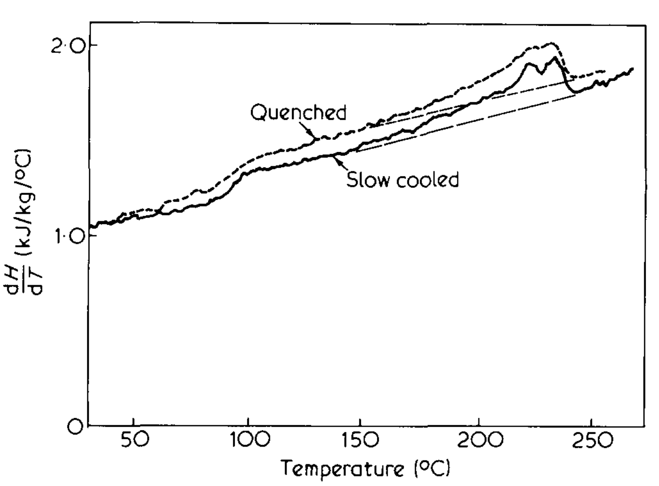

Figure 1 Corrected d.s.c. traces for quenched and slow cooled specimens of polymer A

For one set, the d.s.c. pans were previously heated to 260°C in order to melt the polymer and were then immediately quenched into liquid nitrogen, in order to try to freeze-in the melt structure. For the second set, the pans were previously heated to 260°C and then cooled to room temperature at $1\frac{1}{2}$°C min^{-1}, in order to allow three-dimensional crystallites to form.

X-rays

Samples for diffractometer scans were prepared by loading crumbs of polymer into thin-walled, 2 mm diameter glass capillary tubes. The sample tubes were heated to fuse the polymers (260°C for polymer A and 300°C for polymer B) and then cooled to room temperature. The tubes were mounted on a Philips vertical goniometer inside a hot-stage capable of heating up to 300°C. Scans were obtained in transmission at room temperature and at various elevated temperatures.

Some of the sample tubes were previously cooled slowly from the melt in a controlled oven, while others were cooled quickly by suspending in air in the open laboratory. It was not possible to achieve a more rapid quench without damaging the glass capillary tube.

X-ray photographs were taken as cross-checks. Photographs were also taken of d.s.c.-type samples where it was possible to achieve a very rapid quench.

RESULTS

Thermal analysis

Figure 1 shows typical computer-corrected d.s.c. traces for quenched and slow cooled specimens of polymer A. Despite the computer correction, there is still a remnant baseline curvature which is due to the random run-to-run variation of the instrument. This effect accounts for the small mismatch in the two traces and is particularly exaggerated because of the high sensitivity needed to show up the weak signal. It is worth noting for comparison that the melting peak of well crystallised PET is typically about 20 times higher than the melting process in these polymers.

The traces in *Figure 1* show two clear transitions. There is a slight step at about 90°C associated with the T_g-type of transition. This is followed by a shallow melting process with a final peak at just over 230°C. The general disposition of this process is much the same for both quenched and slow cooled specimens in that the traces are almost superimposable. The main difference is that the slow cooled sample shows more pronounced peaks which are associated with more precisely defined crystals.

The net areas of the melting process were measured by constructing straight baselines from a point just above the T_g process to a point just above the melting process. This procecure was adopted in order to avoid confusion from recrystallisation occurring during the scan. It has been found to work well with PET where the recrystallisation problem is well known[3].

Accordingly the peak areas should be a measure of the net fusion enthalpy that is needed to melt any crystals that were present at room temperature at the beginning of the scans.

Despite the widely different cooling conditions of the polymer A samples, the area of the melting peaks were found to be essentially the same value of 7 ± 1 kJ kg^{-1} for the quenched and slow cooling. The peak areas for polymer B were smaller still at 4 ± 1 kJ kg^{-1}.

X-ray diffraction

Figure 2 shows X-ray photographs of two samples of polymer A. The first in *Figure 2a* is for a sample that has been quenched into liquid nitrogen and shows broad haloes that are reminiscent of conventional amorphous polymers. The second in *Figure 2b* is for a slow-cooled sample with slight orientation, which clearly shows the presence of sharp diffraction lines superimposed on the haloes. *Figure 3* shows a similar pair of photographs for hand-drawn fibres of polymer A, that in one case has been quenched and in the other case has been partially crystallized by annealing at 190°C. A comparison of the patterns shows that the sharp diffraction lines in *Figure 2b* are related in the fibre pattern in *Figure 3b* to the (*hkl*) off-axis (reflections as well as to (*hk*0) equatorial reflections and (00*l*) meridional reflections. Thus one can conclude that the sharp lines in unoriented specimens are associated with crystallites with three dimensional order.

The high degree of orientation exhibited in *Figure 3* is believed to be a good indication of the degree of chain alignment found in local regions of unoriented specimens.

It is very difficult, with these liquid crystal polymers, to make samples without some degree of local orientation on a scale comparable to the size of an X-ray beam. However, photographic checks showed that the samples prepared for the diffractometer had only a minor net orientation, indicating that the diffractometer scans are a reasonable representation of a diffraction profile from a sample of randomized orientation.

Figure 4 illustrates a selection of the diffractometer scans obtained from polymer A. The first two curves were taken at room temperature from samples that had been quench-cooled in air and slowly cooled respectively. The fast cooled sample gives a relatively featureless scan, whereas the slow cooled sample shows clear diffraction lines. The third scan on *Figure 4* is from the slow cooled sample after it had been heated to 220°C and shows the same diffraction lines at reduced intensity and shifted to smaller angles. The reduced intensity is consistent with the d.s.c. trace in *Figure 1* in that at 220°C approximately half of the crystalline melting has occurred. Finally, the fourth scan in *Figure 4* is at 260°C and represents the diffraction profile for the liquid crystal molten state.

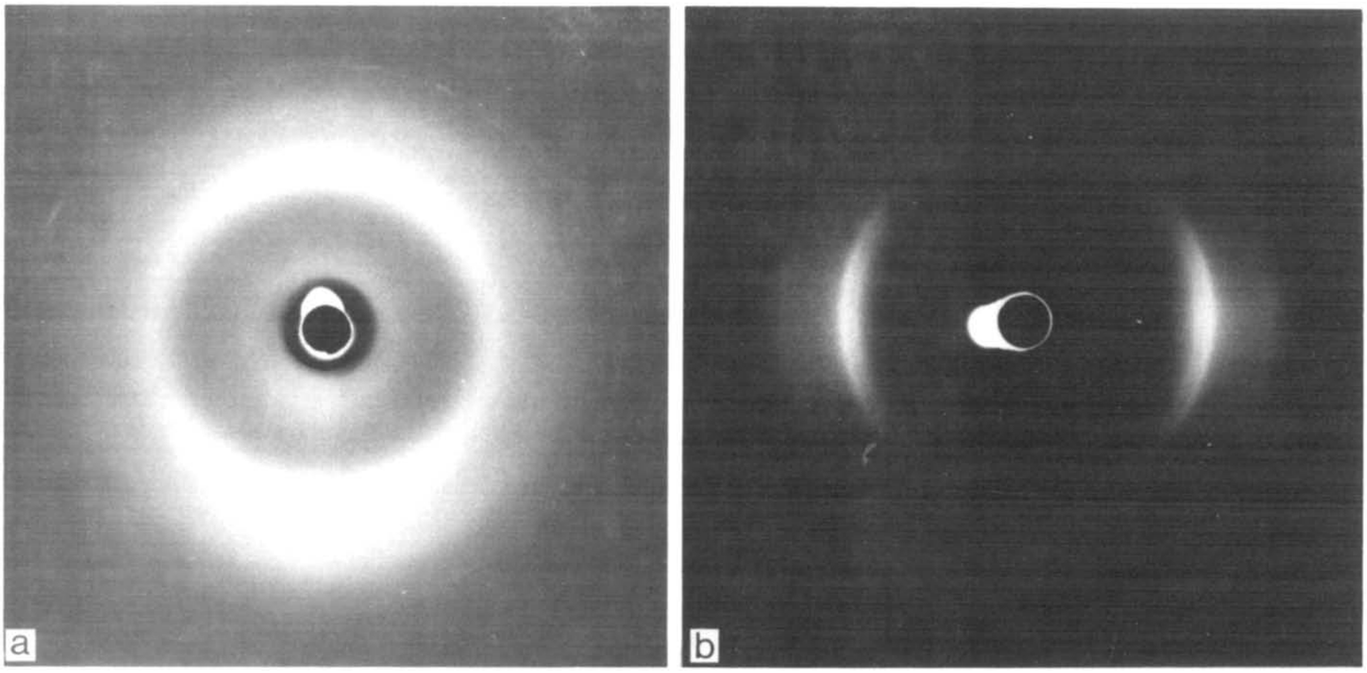

Figure 2 X-ray photographs of polymer A. (a) After quenching into liquid nitrogen; (b) after slow cooling. (The faint spotted outer ring originates from an inorganic impurity.)

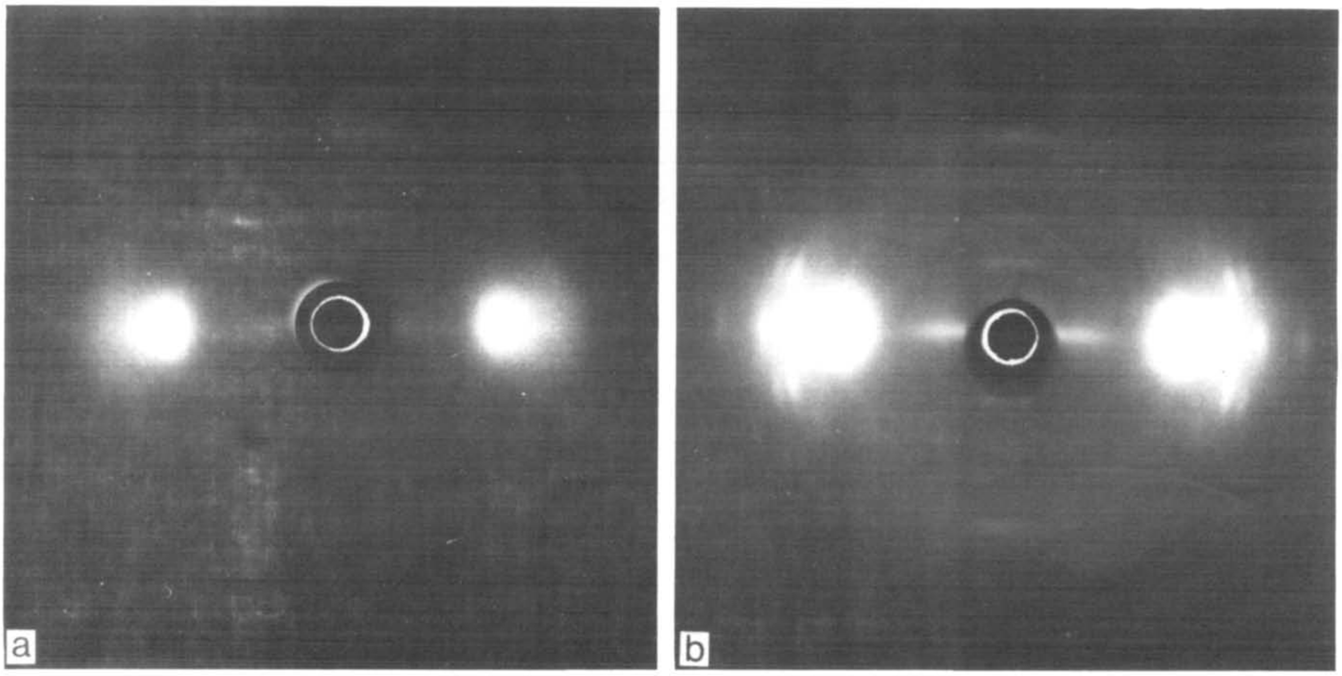

Figure 3 X-ray photographs of hand-drawn fibres of polymer A. (a) After quenching; (b) after annealing at 190°C for 15 min

Estimates of the percentage of three-dimensional crystallinity were made using the approach that has been successfully used for many conventional crystalline polymers. First a flat baseline was constructed from $2\theta = 10^\circ$ to 36°. The melt profile of curve (d) was then scaled down and fitted under the crystalline peaks in the other profiles as shown by the broken lines in *Figure 4*. In order to do this, a certain amount of judicious shifting along the 2θ axis was necessary to account for thermal expansion of the structure. The curves for the slow cooled specimen were relatively easy to fit with the scaled-down melt profile. The fast cooled profile was more difficult on account of the ill-defined diffraction peaks and is thus more tentative. Measurements were made of the area C above the broken line, and the area A below the broken line. The crystallinity was then calculated from the quantity $\frac{C}{C+A} \times 100$. The estimates based on the room temperature scans of the slow cooled samples are given in *Table 1*.

The broadening of the diffraction peaks indicates the difference in crystallite size between the quenched and slow cooled samples. The dominant peak is associated with an ($hk0$) reflection so that its broadening is linked to

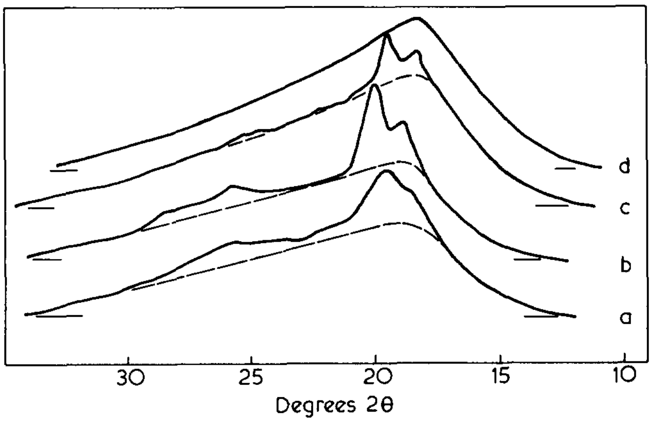

Figure 4 X-ray diffraction curves for polymer A. (a) Air quenched specimen at room temperature; (b) slow cooled specimen at room temperature, and after heating to (c) 220°C, and (d) 260°C

the crystal size in the lateral direction. The Scherrer equation indicates from curve (b) for the slow cooled sample that the crystals are about 10 nm across. For curve (a) from the air-quenched sample where it is difficult to define the peaks, the broadening suggests crystals about 5 nm across. However, in photographs from the quenched d.s.c. samples, any crystalline peaks have been so broadened that it is not possible visibly to distinguish them from conventional amorphous patterns. This infers that if crystals are present in these samples they must be significantly smaller than 5 nm.

Heat of fusion

The X-ray crystallinities can be combined with the area of the d.s.c. melting peaks in order to obtain values for the heat of fusion of a unit mass of three dimensional crystals (ΔH_F). Results based on data from the slow cooled samples are listed in *Table 1* along with a value for the conventional polyester PET. *Table 1* also lists values for the entropy of fusion $\Delta S_F = \Delta H_F / T_m$.

DISCUSSION

Crystallite size

The X-ray and d.s.c. data raise a paradox. On the one hand one finds that the d.s.c. traces are very similar and give almost identical values for the peak areas and for the final melting peaks. On the other hand, the X-ray photographs taken from d.s.c. pans before the runs show the quenched material to be apparently amorphous and the slow cooled material to possess well developed three dimensional crystallinity. How can these facts be reconciled? The most plausible answer is to suppose that the quenched material contains crystals that are so small that they are unable to give sharp diffraction lines. In this way, a fast quenched sample could be mistaken as 'amorphous' while at the same time exhibiting a melting endotherm of similar area to a slow cooled sample with well developed crystals. This answer, however, raises another problem. In order to be mistaken for amorphous material, crystallites would be expected to be less than 30 Å across. Our knowledge of conventional crystalline polymers would suggest that the surface energy contribution would then be so large that both the melting point and the effective heat of fusion, Δh per unit volume of a small crystal, would be significantly reduced from that of a very large crystal, i.e.

$$\Delta h = \Delta h_\infty - \frac{A}{V}\gamma$$

where Δh_∞ = heat of fusion per unit volume of an infinite crystal; A = surface area surrounding regions of three-dimensional crystals; γ = surface energy per unit area; V = volume of crystals.

The proposition we wish to make is that in these liquid crystal polymers, the surface energy, γ, is much smaller than the values observed for conventional polymer crystals. This would enable very small microcrystals to exist where the surface term $\frac{A\gamma}{V}$ will remain negligibly small compared with Δh_∞, thus causing a negligible reduction in the observed heat of fusion.

We would further propose that the small value of γ is a direct consequence of the molecular morphology of the nematic liquid crystal state. In conventional polymers with a lamellar crystal morphology, the surface energy is dominated by the fold surface energy which can be attributed to three main contributions:

(i) The interfacial energy associated with the difference in binding energy on the two sides of the phase boundary.

(ii) Strain energy from sharply folded molecules and from an accommodation of the mismatch in density on crossing the fold surface.

(iii) Restrictions in entropy of the free parts of chains that are attached to the crystal at the fold surface, e.g. loops and loose chain ends.

In contrast to this, it is envisaged that in nematic liquid crystal polymers there will be little change in the general configuration of the molecules before and after melting. As indicated in the sketch in *Figure 5*, this contrasts markedly with the vast increase in disorder experienced when a conventional lamellar crystal melts. Thus, in a nematic polymer system, we can expect the above contributions (ii) and (iii) to the surface energy to become small compared with the interfacial contribution (i). It is common practice to estimate the magnitude of the interfacial energy from the empirical relationship[4]:

$$\gamma = 0.1\ b\Delta h$$

where b = distance between lattice planes.

If we assume that the crystallites in the nematic system are cubic of length a then the ratio $A/V = 6/a$. The surface term in the equation above can thus be reduced to:

$$\frac{A\gamma}{V} \simeq 0.6\ \Delta h \frac{b}{a}$$

Thus one can see that the apparent Δh will remain within 10% of Δh_∞ providing the crystal size $a > 6b$. A crystal of six lattice spacings across is of a size where it becomes difficult to distinguish diffraction from that of an amorphous polymer. However, providing γ has the same value indicated here, then the observed heat of fusion will

Table 1 Comparison of data with conventional PET

Polymer	T_m (K)	X-ray % crystallinity	ΔH_F (kJ kg^{-1})	ΔS_F (kJ kg^{-1} K^{-1})
Polymer A	513	17	40	0.08
Polymer B	563	21	20	0.04
PET	530	Typically 50	135	0.25

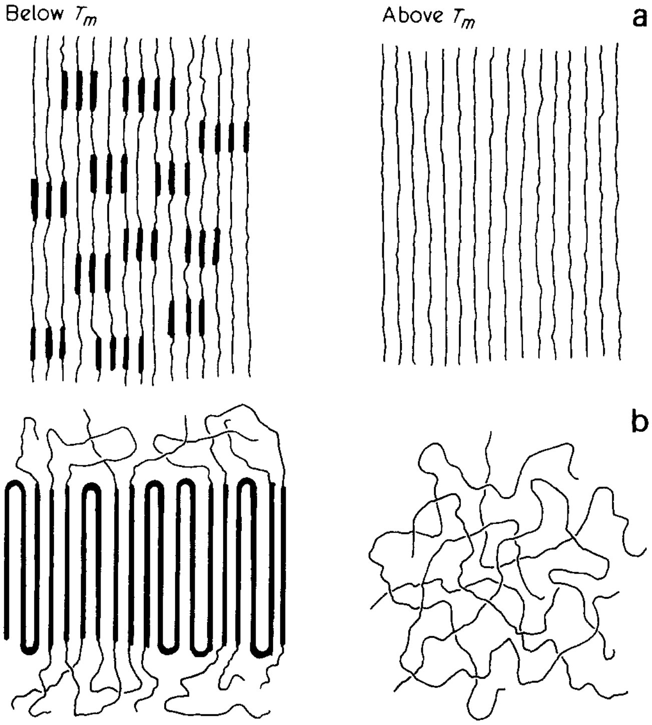

Figure 5 Schematic diagram of the morphologies above and below the crystal melting point for: (a) rigid chain nematic polymer, and (b) conventional polymer with chain folded lamellar crystals. The thicker parts of the lines represent regions where the chains form three-dimensional crystal lattices

for all practical purposes be identical to that of a crystallite of conventional size. If γ were to be similar in value to that usually found for the fold surface of conventional polymers, then the term $\frac{A}{V\gamma}$ would be so large that the crystal would be unstable and would spontaneously melt.

Not only would microcrystals represent a stable equilibrium state in nematic systems but their initial nucleation from the melt will also be much easier and could be almost spontaneous at relatively low under-cooling. However, it should be noted that once the initial crystal nucleation from the mobile nematic melt has occurred, the crystals will immediately prevent the long rigid chains sliding longitudinally so that subsequent growth and perfection of crystal will be retarded.

Thus, we find the nematic chain morphology can lead to a lower γ than in conventional polymer crystals and that this in turn leads to the possibility of more easily nucleating crystals that are much smaller than those found conventionally.

Enthalpy of fusion

Table 1 shows that the enthalpy of fusion ΔH_F per unit mass of the liquid crystal polymers is significantly less than that of a corresponding conventional polymer such as PET. The above discussion has shown that the low ΔH_F cannot be attributed to surface energy effects, since γ is low, thus making ΔH_F independent of crystallite size. The main cause for the lower ΔH_F must be imperfections within the crystal lattice causing poor cohesion of chains. The reason for the imperfection must be the non-regular nature of the copolymers in which there is a low probability of the long runs of regular sequences that are needed for well packed coherent crystals.

Entropy of fusion

The two liquid crystal polymers both melt in approximately the same temperature range as PET. Thus their lower ΔH_F also reflects a much lower entropy of fusion ($\Delta S_F = \Delta H_F/T_m$) than in a conventional polymer. The reduced ΔS_F is a direct consequence of the extra stiffness of the chains and correlates well with the variation in flexibility predicted by their formulae.

The influence of stiffness on chain configuration is dealt with in Flory's classic paper[5]. He showed that as the stiffness is increased, a point is reached where the polymer melt will spontaneously exist in the nematic state rather than as a random coil. If such a nematic system containing crystallites is melted, it is envisaged that there will be no change in the overall chain configuration. The main motions to become available to the chains on melting will be longitudinal translation, chain rotation and minor internal chain motions that are not capable of altering the overall configuration. Thus the change in entropy on melting will be derived from the onset of these motions. A simplified calculation (see Appendix) shows that the entropy change per molar segment of the chains will be given by:

$$\Delta S = \frac{k \ln x}{x} + k \ln r$$

where x = number of segments per chain; r = degrees of internal freedom per segment.

The first term is essentially related to longitudinal translation and is negligible for reasonable molecular weights. The second term derives from the internal chain motions that do not change the overall configuration. If one assigns the size of a segment to a phenyl block of molecular weight about 120, then the results in *Table 1* reduce to segmental entropy changes of 10 $\mathrm{JK^{-1}}$ for polymer A and 5 $\mathrm{JK^{-1}}$ for polymer B. The above $k \ln r$ term achieves these kind of values for with 2 to 3 degrees of freedom per segment. This does not seem unreasonable.

Relevance to design of liquid crystal polymers

It is worth reflecting further on the low values of ΔH_F and ΔS_F in order to emphasize the peculiarities of liquid crystal polymers. As discussed above, the low ΔH_F is directly related to the lower level of molecular cohesion within the crystallites resulting from chain irregularities, whereas the low ΔS_F is a direct consequence of the chain stiffness. Chain stiffness and chain irregularity are two distinct properties that can be separately designed into the molecule.

Chain stiffness is the main property that will determine whether the polymer melt will exist as a nematic mesophase rather than as a conventional isotropic melt. If the melt is nematic, then it automatically follows that there will be a low entropy change since there is no change in overall configuration on crystallizing.

Since $T_m = \frac{\Delta H_F}{\Delta S_F}$, then for a given ΔS_F, T_m will depend on the value of ΔH_F; i.e., on the chain regularity and crystal packing. If ΔS_F is low, then ΔH_F must be made low, otherwise T_m would be too high and the system will become intractable. For example, if polymer A had the same ΔH_F as PET, the melting point would be in excess of 1000°C. Thus, in order to make processable liquid crystal polymers, one must introduce irregularities into the chain in order to limit the effective bonding of the crystals.

As a converse, it is worth adding that a low ΔH_F such at observed in polymers A and B would be of little value in a conventional polymer where the potential ΔS_F is much higher, since then the melting point would be well below room temperature. In fact, crystals with such low ΔH_F can only exist in polymer systems with a nematic morphology where the surface energy γ is low. In a conventional polymer where lamellar crystals grow, the surface energy would be much larger and any crystals with such a low ΔH_F would melt instantaneously.

CONCLUSIONS

It has been shown that the identical heat of fusion for slow cooled specimens with well developed crystals and for quenched specimens with almost amorphous X-ray patterns can be explained by the presence of microcrystals that are much smaller than those possible in conventional polymers. They are able to exist by virtue of a very low surface energy which is a direct consequence of the nematic morphology of the chains.

The low ΔS_F also results from the nematic state of the melt which in turn is a consequence of the chain stiffness. The low ΔH_F is a reflection of the chain irregularities preventing good crystal cohesion and is an essential feature of the design of the molecules. If it were not so low, the T_m would be too high for processing.

ACKNOWLEDGEMENT

I gratefully thank my colleagues at ICI—F. N. Cogswell, B. P. Griffin and M. K. Cox who have been involved in synthesizing and characterizing the polymers and to B. N. Osborne who has assisted in the measurements described here.

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APPENDIX

Entropy change at crystal–nematic transition

Since the molecular configuration is unchanged there is no need to calculate the configuration of any individual molecule. There are only two factors to consider:

(i) the number of positions in which any molecule can be placed. This will be defined by counting the number of places that the first segment of any molecule can occupy.

(ii) the number of configurations that any individual segment of a chain can take up without changing the configuration of the chain as a whole. This could involve rotational movements of a segment or group of segments. It will be accounted for by assuming there are r degrees of freedom for each segment.

It is convenient to follow the classical Flory approach using a lattice to represent possible sites for molecular segments[5]. There are n_0 lattice sites, n_2 identical polymer molecules composed of x segments.

Consider the stage where the first j molecules have already been placed on the lattice.

There are therefore $(n_0 - xj)$ possible sites for the placement of the first segment of the $(j+1)$th molecule.

Then the number of configurations of the $(j+1)$th molecule

$$= (n_0 - xj)\, r^x$$

Therefore the total number of ways of arranging all n_2 molecules

$$= \prod_{j=0}^{j=n_2-1} (n_0 - xj) r^x$$

$$= r^{n_2 x} x^{n_2} \left(\frac{n_0}{x}\right)!$$

Since the n_2 molecules are identical, the total number of distinguishable configurations

$$\Omega = \frac{r^{n_2 x} x^{n_2} \left(\frac{n_0}{x}\right)!}{n_2!}$$

$$= x^{n_2} r^{n_2 x}$$

In the solid state, we assume the molecular configurations are the same as the melt; the molecules are fixed in one position and they are unable to rotate. Therefore Ω represents the increase in the number of configurations on melting. The change in entropy is therefore:

$$\Delta S \sim k \ln \Omega$$

$$= k\{n_2 \ln x + n_2 x \ln r\}$$

Therefore entropy change per a segment is

$$\frac{\Delta S}{n_2 x} = k \frac{\ln x}{x} + k \ln r$$