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A study on the achievement of high-modulus polyethylene fibres by drawing

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Several methods of preparing spherulitic sheets of high-density polyethylene from which high draw ratios (~ 30x) and high moduli (~ 800 kbar) may be obtained are described. It is shown that, independent of the method of preparation of the initial sheet, and provided certain conditions are met, the modulus is a unique function of draw ratio. The maximum draw ratio (and hence modulus) achievable from a particular sheet is shown to depend on its morphology and its molecular weight distribution; in particular, the presence of some segregated low molecular weight material appears to be essential. When viewed in the polarizing microscope a "black" region often is observed bounding the spherulites, particularly in those sheets which give high draw ratios. This region is correlated with segregated low molecular weight material. In addition, the recovery properties of high modulus fibres are reported, both after isothermal strain and on annealing when near complete recovery is observed.

1. Introduction

Currently there is an upsurgance of interest in fibres of exceptionally high draw ratios (i.e. to $> 15\times$) which arises from the renewed quest for high moduli. In the case of polyethylene, the polymer in which there is at present most interest, the theoretical modulus (~ 3 Mbar) is reasonably well known [1], nevertheless this has not been achieved in the usual cold-drawn material (drawn up to ~ 15x) despite the very high degree of molecular orientation obtained by such drawing. Draw ratios of up to ~ 40x have featured in the literature before [2–5] but to our knowledge these studies were not connected with the search for high moduli. It is due to the recent developments of Capaccio and Ward [6] that the two objectives of extremely high draw ratios and moduli have become indisputably linked. They have announced that provided certain criteria for molecular weight, initial morphology and drawing conditions are satisfied elongations of up to 30x can be achieved, along with moduli of up to 700 kbar (i.e. up to ~ $\frac{1}{4}$ to $\frac{1}{3}$ of the theoretical maximum).

Capaccio and Ward compared the drawing characteristics of several commerical polyethylenes, and concluded that for optimum result the molecular weight has to be low and the distribution narrow. In addition they concluded that the process was dependent on the initial morphology, and that the most favourable morphology, was achieved by slow cooling to 110° C and then quenching. Further, although no special point is made of it, it appears that an elevated drawing temperature and a fast draw speed are also required.

It will be apparent that the above criteria are very broad which makes it unlikely that conditions for achieving high modulus by high draw ratios should be very critical. Concerning the molecular weight criterion the commerical samples examined by Capaccio and Ward vary both as regards their molecular weight distribution and their various averages and it is by no means clear which if any is the decisive factor. As regards the morphology, non-isothermal crystallization always leads to a complex end-product and, therefore, it would be very coincidental if the particular treatment established by Ward and Capaccio led to a uniquely desirable morphology not achievable also along other routes. Finally, as already stated, it is not evident from their paper to what extent the process is dependent upon the exact drawing temperature; consequently we undertook similar experiments. First we attempted to reproduce their effects and then to vary the appropriate conditions according to our own design. For this we chose the commercial grade Rigidex 50 which gave the best results in the Capaccio and Ward experiments. For the study of the effect of morphology we varied the crystallization conditions of the starting material in the ways to be described, and similarly varied the drawing conditions (temperature, draw rate and time of draw). Although systematic variations in the end results were observed we state at the onset that we were surprised by the relative ease by which high-modulus material – coveted over so many years in the past – could be obtained. For the examination of the molecular weight effect we used one and the same starting material but modified its distribution by removing the low molecular weight portion and in a further experiment reconstituting it. In the course of all these experiments we examined the starting material with the polarizing microscope. This in itself may not appear novel, nevertheless out of the variety of features displayed by the visual image we attempted to extract information which may form a common underlying trend. In order to facilitate interpretation in molecular terms we also used a completely different kind of starting material, namely single crystal mats of the above polymer, where the initial morphology is known with reasonable certainty, and performed drawing experiments on these mats.

In the course of all these examinations we also noted and studied the recoverability of strain, both under isothermal conditions following the stress–strain measurements and on raising the temperature.

2. Experimental

2.1. Preparation of sheets

Seven types of sheets of polyethylene were made using various preparation techniques. In all cases the starting polymer came from the same batch of Rigidex 50 high-density polyethylene; however, in two cases the molecular weight distribution of the material was deliberately altered, as will be described below. The seven sheets consisted of one single crystal mat, four spherulitic sheets each with a different preparation and morphology, and two additional spherulitic sheets made from the modified polymers but otherwise prepared identically.

The single crystal mats were prepared as follows: 0.01% solution of Rigidex was crystallized in xylene at 80° C using the self seeding method [7] the seeding temperature being 103° C. The resulting suspension was filtered at room temperature producing a coherent oriented mat in the usual manner.

The spherulitic sheets were obtained by melting the polymer in a press at 160° C and then subjecting it to one of the following treatments: (1) direct quenching in cold water, to be referred to as Q-type, (2) direct quenching in cold water followed by annealing at 125° C for 2 h (to be referred to as A-type), (3) cooling, at $\sim 15^\circ$ C min^{-1} to 110° C and quenching in cold water, optimum condition according to Capaccio and Ward (sheets made this way to be referred to as S_1-type), (4) cooling at $\sim 1.5^\circ$ C min^{-1} to $\sim 110^\circ$ C and then quenching in cold water, to be referred to as S_2-type.

The molecular weight modification was achieved by fractionating crystallization. The polymer was crystallized in xylene at 90° C and filtered at that temperature. The filtrate contains the low molecular weight end of the distribution. The corresponding G.P.C. traces are shown by Figs. 1 and 2. As seen from Fig. 2 most of the low end of the distribution below ~ 2000 mol wt is removed. Fractionation by this method has been documented in detail elsewhere [8]. The resulting filtrate was dried in vacuum oven at 80° C and sheets, to be termed L-type, were prepared as under 3. In a similar preparation the crystal suspension was not filtered at 90° C but allowed to cool to room temperature when all material, not yet crystallized at 90° C, precipitates. Filtration was then carried out at room temperature. This filtrate has the same molecular weight distribution as the starting material (gave same chromatogram as Fig. 1) and can be considered as the material first fractionated by crystallization at 90° C as above, but subsequently reconstituted to its original molecular weight distribution. Sheets were again pressed by method 3 to be termed R-type. The processing temperature for both solution precipitated samples was kept deliberately low (140° C) to avoid the possibility of degradation which may arise due to the re-

TABLE I Summary of methods of preparation of sheets

Sheet type	Preparation
Q	Melt 160° C, quench
A	Melt 160° C, quench, anneal
S_1	Melt 160° C, cool at 15° C min^{-1} 110° C, quench
S_2	Melt 160° C, cool at 1.5° C min^{-1} 110° C, quench
L	Hot filter, melt 140° C, cool at 15° C min^{-1} 110° C, quench
R	Cold filter, melt 140° C, cool at 15° C min^{-1} 110° C, quench

moval of antioxidant during dissolution. The details of preparation of all types of sheet are summarized in Table I.

2.2. Drawing of fibres

The single crystal mats were drawn manually using tweezers to grip the samples, which were small strips cut out from the mats. The mats only became extensible in the temperature range 90 to 110° C. As far as possible the mats were drawn at the lower end of this range. In this way extensions of up to 35x were obtained.

The spherulitic sheets were drawn in an oven using an Instron tensile testing machine. For this purpose tensile test specimens with a gauge of 1 cm and a width of 0.25 cm were stamped from the sheets, (the thickness of the A, Q, S_1 and S_2 sheets was ~ 0.13 cm and that of the L and R-types ~ 0.10 cm). These specimens were then drawn at a rate of 5 cm min^{-1} at a constant temperature in the range 70 to 110° C (N.B. the temperature within the oven varied by up to ± 2° C during the drawing process).

2.3. Quality Control

In order to achieve a degree of consistency in the drawing process, and in the subsequent modulus measurements strict "quality-control" conditions were imposed on the samples. Firstly all specimens were examined before drawing using optical microscopy and density measurements for any inhomogeneity (e.g. cracks, inclusions etc.), their thickness and width checked for uniformity and their edges checked for smoothness. If any fault was found then the specimen was rejected; about 1 specimen in 20 was rejected as a result. After drawing similar checks were carried out. In particular specimens were checked for uniformity of draw ratio. Of these drawn specimens only about 1 in 5 was acceptable. In addition it was required that the aspect ratio of the samples was at least 100:1 before modulus measurements were carried out. This was necessitated by the recent recognition [9] that end effects due to the grips (St. Venant's principle) can be very large in highly anisotropic samples which unless very large aspect ratios are taken will falsify the modulus measurements details to be reported elsewhere [14].

2.4. Measurement of modulus

The tensile modulus of all the acceptable samples was measured using an Instron tensile testing machine, at an (initial) strain-rate of $10^{-4}\,\text{sec}^{-1}$ at room temperature. The moduli were then calculated from the load elongation curve using the stress at 0.1% strain (Figs 3 to 5). In addition the 10 sec moduli of some samples were measured using dead loading techniques. These results are plotted on Fig. 6 and are in good agreement with

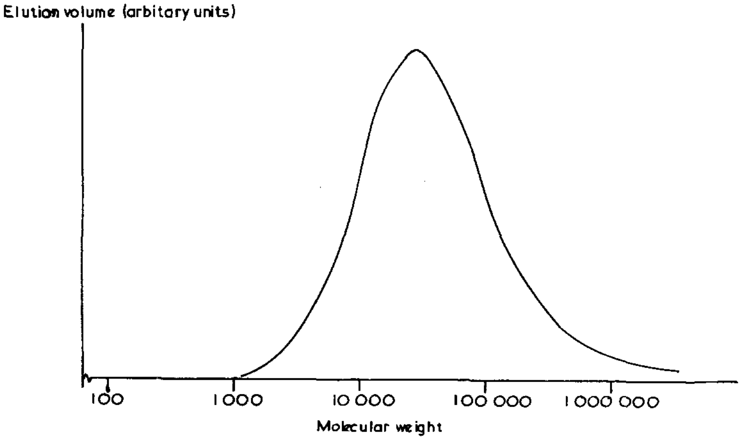

Figure 1 G.P.C. trace of Rigidex 50 as supplied sheet types A, Q, S_1, S_2 and R.

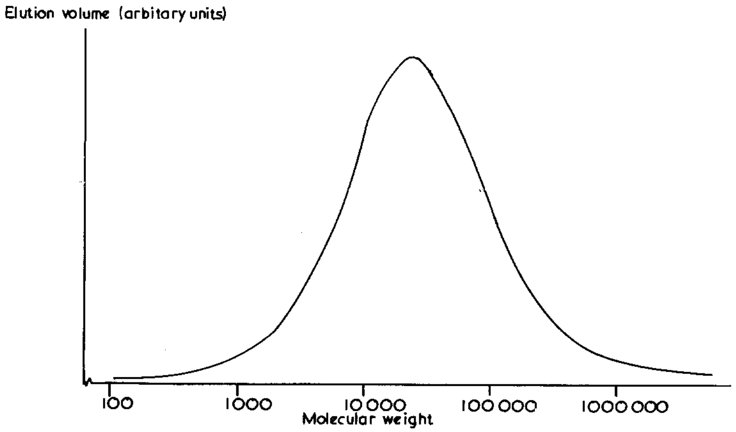

Figure 2 G.P.C. trace of Rigidex 50 with low molecular weight removed as described in the test and used for L-type sheets.

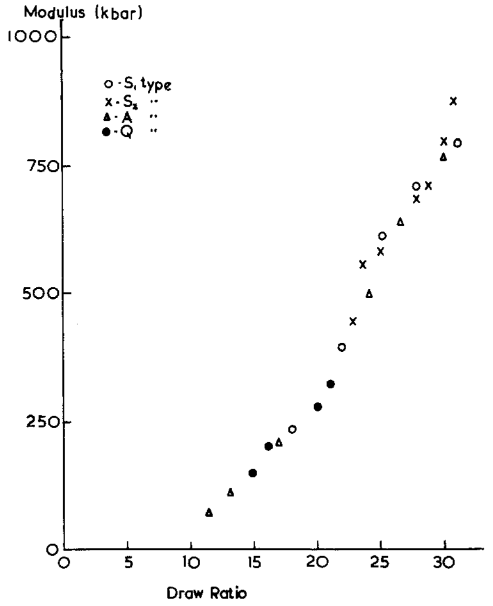

Figure 3 Graph of modulus versus draw ratio for drawn single crystal mats.

the Instron stress–strain curve.

3. Results

3.1. Modulus

The moduli of the drawn single crystal mats are plotted against the draw ratio in Fig. 3. The large error bars result from difficulty in measuring accurately the thickness of these very thin drawn samples (NB the thickness is needed to compute the cross-sectional area which is used to calculate both the draw ratio and the modulus). Nonetheless a distinct upward trend of modulus with draw ratio may be clearly seen and it appears that under the preparation and selection conditions defined above that the modulus is a unique function of draw ratio.

The results for the A-, Q-, S_1- and S_2-Type drawn spherulitic sheets are, however, much more convincing in this respect. These moduli are plotted against draw ratio in Fig. 4. It is quite clear from Fig. 4 that, provided the quality-control procedures defined above are strictly adhered to, the moduli of all these samples, prepared from sheets with different morphologies, are a unique function of the draw ratio. Samples which had been rejected on the grounds of non-uniform draw ratio, even allowing fairly large errors in draw ratio, did not fit the curve in Fig. 4, the measured "moduli" being well below the values for uniform specimens.

It can also be seen from Fig. 4 that only certain sample types of initial sheets gave the unusually high draw ratios and correspondingly high moduli. Thus the "Q-type" samples proved very difficult to draw to extensions greater than 16x ; despite many attempts only two specimens with draw

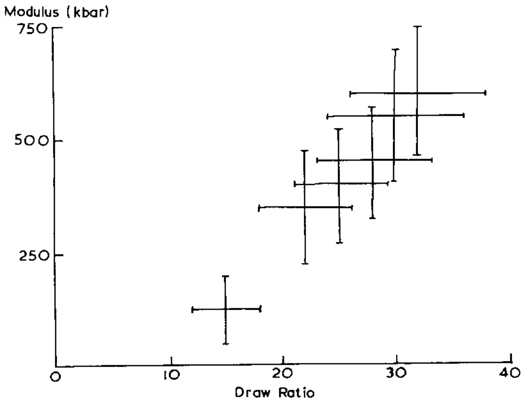

Figure 4 Graph of modulus versus draw ratio for drawn spherulitic sheets (types A, Q, S_1 and S_2).

TABLE II

Specimen type	Draw temperature	Draw time (sec) (draw speed = 5 cm min^{-1})	Draw ratio	0.1% modulus (kbar) (av. of 3 measurements)
A	75 ± 1.0	120	24.0	505 ± 20
A	85 ± 1.5	90	26.4	690 ± 20
A	96 ± 1.0	120	29.9	775 ± 25
A	21 ± 0.05	60	8.5	40 ± 8
A	53 ± 1.5	60	11.3	70 ± 15
A	67 ± 1.5	120	12.9	120 ± 10
Q	85 ± 2.0	90	16.0	210 ± 20
Q	96 ± 1.0	90	20.0	285 ± 25
Q	76 ± 1.5	90	21.1	330 ± 25
Q	74 ± 2.0	90	14.8	160 ± 15
S_1	76 ± 2.0	120	28.1	770 ± 15
S_1	78 ± 1.5	120	31.0	800 ± 25
S_1	83 ± 1.0	120	25.5	620 ± 20
S_1	72 ± 2.0	120	22.2	330 ± 15
S_1	65 ± 1.5	120	17.9	240 ± 10
S_2	77 ± 1.5	120	28.8	710 ± 20
S_2	76.5 ± 1.5	120	25.1	584 ± 20
S_2	74 ± 2.0	120	30.7	880 ± 25
S_2	76 ± 2.0	120	22.9	448 ± 20
S_2	77 ± 2.0	120	28.0	688 ± 25
S_2	79 ± 2.0	120	23.7	555 ± 20
S_2	76.5 ± 1.5	120	30.1	795 ± 25

ratios higher than this were satisfactorily produced (these have draw ratios of 20 and 21). It is to be noted that both these were produced at temperatures towards the upper end of the range used (85 and 96° C respectively) (Table II).

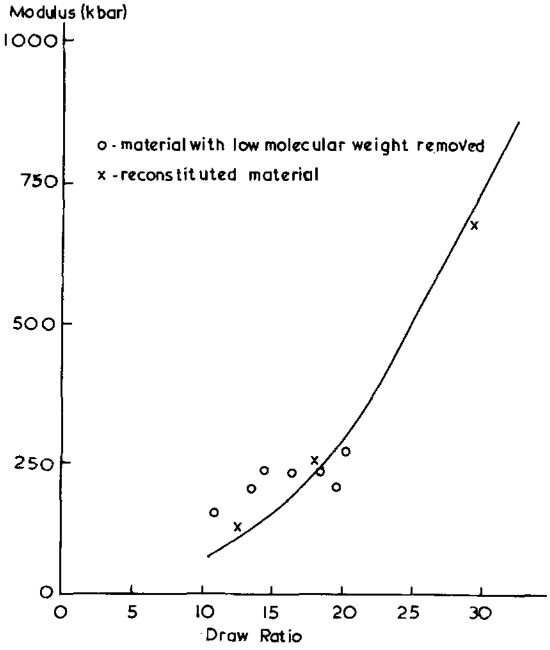

Figure 5 Graph of modulus versus draw ratio for sheet types L and R (the line on this graph is taken from Fig. 4).

As seen there is a consistent dependence of modulus on draw ratio. This does not mean, however, that a given draw ratio could be consistently achieved under nominally identical conditions, and further that there was a consistent dependence between drawing conditions and the ultimate draw ratio achieved. Thus all the S_2 samples were drawn using as near identical conditions as possible, these conditions having been determined as those which gave the most repeatable results in previous experiments (draw speed of 5 cm min^{-1} for 2 min and a temperature of 75 ± 2° C), however as can be seen from Fig. 4 the draw ratios achieved varied between 23 and 31x. For information a full list of the drawing conditions used for all specimens in Fig. 4 is included (Table II).

The moduli of the L- and R-type samples are plotted against draw ratio in Fig. 5; the line drawn on this graph is taken from the 0.1% modulus measurements plotted in Fig. 4. The L-type material does not follow that line while the R-type does, which implies that the reconstitution and subsequent processing have left the polymer by and large unchanged, while the removal of the low molecular weight material has had an effect on the drawing characteristics of the polymer. At low draw ratios the L-type material shows higher

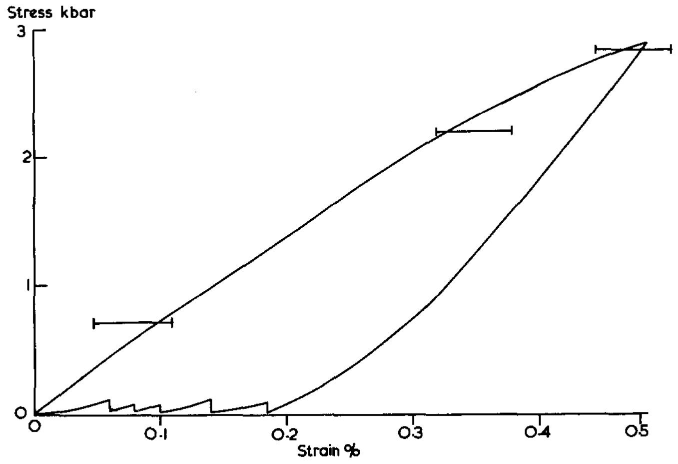

Figure 6 Stress–strain curve of an S_1-type sample with draw ratio 28.1, including strain cycling. The horizontal bars refer to the dead loading experiments.

TABLE III

Sheet type	Size of spherulites diameter (μm)		Diameter of rows (μm)	Depth of rows (μm)	% of spherulites showing black-line (estimate)
	average	range			
Q	12	4–20	20	~60	15
A	16	12–25	v. few 15	80	80
S_1	20	8–30	absent	–	90
S_2	5	2–15	absent	–	(very difficult to observe due to small size of spherulites) 40
L	12	4–20	absent	–	25
R	10	5–15	v. few 15	50	85

moduli than any of the other samples used, however at a draw ratio of about 18× the modulus of the L-type sample coincides with that of the rest, and the impression is given that for still higher draw ratios (only 20× could be satisfactorily achieved for the L-type sample) the curves may cross.

3.2. Morphology of sheets

Examination with the polarizing microscope revealed a multitude of features, which differed from one sample to another. Three of these, the spherulitic size, the presence and frequency of black boundaries observed around some of the spherulites (such as shown by Fig. 7) and row nucleated structures are recorded in Table III. The black boundaries referred to are regions around the spherulites which appear black for all orientations with respect to the polarizer; this indicates that the material in these regions is either amorphous or consists of disoriented crystallites. These regions usually give the appearance of a thin black line surrounding a spherulite and will for the sake of brevity be referred to simply as "black-lines".

As can be seen from the table, there appears to be some correlation between the number of spherulites with the black-lines and the maximum achievable draw ratios (N.B. only the L-and Q-type samples do not give high draw ratios and both these show distinctly less black-line effect than the A-, S_1- and R-types. The S_2-type has such small spherulites compared to the other types that the presence of the black-line is difficult to determine (the figure of 40% is a rough estimate based on the appearance of the larger spherulites). We believe that the correlation of the frequency of black-lines and the modulus may be significant. It appears that the black-line may be due to low molecular weight material, which in the case of S_1

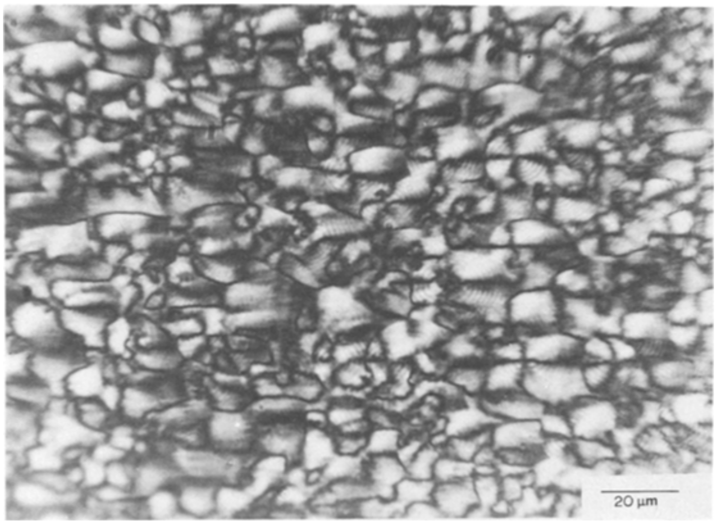

Figure 7 Photomicrograph taken between crossed polars of a section of A-type sheet showing the black line around spherulites.

and R samples remained uncrystallized on slow cooling to 110° C and accumulated along the spherulite boundary, while in the case of the A-type it may have been ejected to the spherulite boundaries on partial melting followed by recrystallization during annealing.

3.3. Elastic behaviour

Fibres produced from the S_1-type sheets and some from the A- and S_2-types show interesting stress–strain curves as illustrated by a typical curve in Fig. 6. These fibres show strain softening and yet the strain is fully recoverable. This effect has been observed in some fibres for strains of up to 7%; it has not yet been investigated at higher strains due to technical problems with gripping these fibres. The bars in Fig. 6 are the results of the 10 sec dead-loading experiments described in the introduction and serve to show the compatibility of these two ways of measuring tensile modulus. The vertical lines on Fig. 6 occur where the return of the cross-head of the testing machine was stopped as zero load was approached, and not restarted for some time (up to 1 h).

3.4. Retractibility of the fibres

All these highly drawn fibres show a remarkable contraction on heating close to the melting point [10], as illustrated in Fig. 8a. The measurements were carried out using a small fibril torn from the macroscopic fibre which was floated on silicon oil in a Mettler microscopic hot stage and observed in the optical microscope. The thermogram (Fig. 8b) was obtained using a similar fibril in a Perkin-Elmer Differential Scanning Calorimeter. Recrystallizing and remelting the fibre in the DSC showed that there was some superheating, about 4° C, present in the fibre; however, whether this is due to some structural properties or some constraint preventing the fibril from contracting is not yet established. It is to be noted that the drastic retraction occurs nevertheless before the majority of the material is molten (compare Figs. 8a and b).

4. Discussion

Two qualitative conclusions emerge at first sight. Firstly, that the prerequisite for ultra high (i.e. near theoretical) modulus in an as drawn material is a very high draw ratio which perhaps significantly is in the range of 30×. This has already been announced and is the principal contention of the work by Capaccio and Ward. While there are certainly trends which facilitate or impede it, the required draw ratio, and with it the high modulus, can be obtained under a variety of circumstances and there is no critical condition which has to be strictly adhered to. From our experiments, the most stringent condition which emerges is the presence of some very low molecular weight material. Beyond that the broad requirements are high temperature of drawing and slow crystallization of the starting material.

Quantitatively, the most conspicuous feature is the unique correspondence between draw ratio

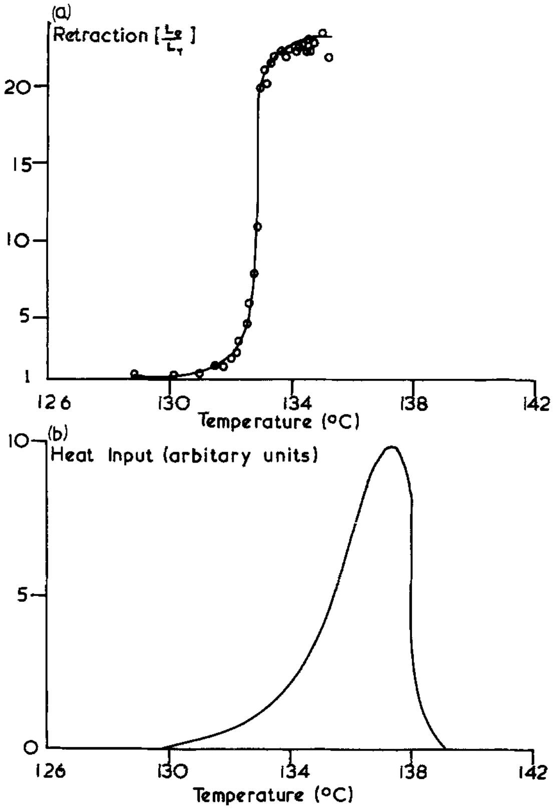

Figure 8 (a) Graph showing retraction of the same specimen used in Fig. 6 after 30 sec at the elevated temperature. (b) Thermogram of the same sample as in (a).

and modulus over the entire range of draw ratios as revealed by Figs. 3 to 5. We see that there is a master curve which is followed by samples with different initial crystallization treatments. Strictly, however, this master curve only holds for samples of the same molecular weight composition: it is not quite obeyed by the sample depleted from its low molecular weight end but the standard behaviour is re-established once the starting molecular weight has been reconstituted. Neither is the uniqueness of the master curve upheld in the case that the starting sample, while having the same molecular composition, is of entirely different preparative origin as shown by the behaviour of the single crystal mats. Here the modulus versus draw ratio curve is somewhat below that corresponding to the melt pressed films. Even so, in view of the entirely different sample preparation procedure the similarities are more noteworthy than the differences, particularly as the mats were drawn at higher temperatures than most of the films (90 to 110° C).

At first sight there is no self-evident reason why better developed crystallites formed on slow cooling or on annealing of the quenched specimen should yield higher ultimate draw ratios. Nevertheless the requirement of slow crystallization may tie up with the requirement of having low molecular weight material present in the following way. During fast cooling, low and high molecular weight will crystallize together, during slow crystallization or annealing there is the possibility of segregation. In particular, at 110° C all except the shortest molecules will have already crystallized. The observation by Capaccio and Ward that it makes a difference whether quenching is performed first to 110° C or directly to lower temperature implies that the incorporation, or alternately the segregation, of these shortest molecules has an important part to play. There is evidence to support the view that segregation does occur in sheets which may be drawn to high extensions: Fig. 2 of [6] shows the density of sheets as a function of their quenching temperature; the variations observed may be attributed to segregation effects. In addition, Smith *et al.* have observed a narrow line in the nmr spectra of such sheets which they have attributed to the segregation of low molecular weight material during crystallization [11]. Our observations confirm that in sheets which are slowly cooled segregation does occur, furthermore our experiments on total removal of this lowest molecular weight fraction indicate that the presence of these short molecules in segregated form is necessary for the achievement of high draw ratios. It follows that the low molecular weight material is needed but this in its segregated form.

At this point we invoke the observations on the black-line between spherulites. To all indications this corresponds to segregated low molecular weight material accumulated along the spherulitic boundaries which, even if it did crystallize on cooling, did not do so coherently with the spherulites but only in a random microcrystalline fashion thus forming a zone which is distinct from the spherulite itself as seen between crossed polaroids. If this argument is relevant at all it would mean that the nature of the spherulitic boundaries could be significant; a point which is being pursued.

Concerning the molecular mechnism only a few comments will be made. Clearly, as already expressed by Capaccio and Ward, we would expect the chains to be highly extended. The experiments on the single crystal mats are noteworthy in this respect. Namely, here we know for certain that we have chain-folded crystals which we are pulling laterally. As the crystals are about 120Å thick and their interchain separation is 4 to 5Å, 30x extension should correspond to complete pulling out of chains [12]. Thus in this case we can state with reasonable confidence that we are dealing primarily with fully pulled-out folds*. Nevertheless even in this case the pulling-out of folds cannot be quite complete otherwise there would be no complete retraction on heating as indeed there is none in crystals actually formed from pre-extended chains by primary crystallization. Hence some memory of the original folded structure must persist. This could be in the form of residual folds or kinks. We do not speculate on this issue further beyond restating the point we made elsewhere [10], namely that high degree of chain extension when obtained by deformation of material which is crystalline to begin with is always recoverable while that due to crystallization from pre-extended molecules is not. This means that there must be locked in stresses in the former. Extended chains should provide the near theoretical modulus irrespective of how the extension has been achieved. Nevertheless, it is noteworthy that the best, and certainly the most readily achievable results so far have been obtained along the former route leading to material where the extension is thermally recoverable. Whether a matter of principle is involved or, what appears more likely, it is merely a matter of practicalities that the solid-state drawing method has led to these results before others, needs yet to be seen.

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* A 30 to 40x extension within smooth (i.e. block-free) fibres arising by lateral deformation of single crystals could be directly deduced in electron micrographs where vacuum-deposited gold particles served as strain markers [13]. As the corresponding macroscopic mats could be extended by the same amount it seemed reasonable to suppose that the full extension itself is due to the pulling out of the crystal layer.