Orientation processes in the drawing of dry gel films of polyethylene and polypropylene

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Changes in the orientation with draw ratio of dried gel films of high density polyethylene and isotactic polypropylene were monitored by polarizing microscopy, birefringence measurements and X-ray diffraction. The results suggest that the gels, formed from 0.5 or 1% w/v solutions, contain a continuous gel network within which the bulk of the crystallized polymer is held. Tie molecules link the initial gel network with the crystalline morphology formed as the gel cools. The distribution of tie molecules is suggested as the reason why the undrawn gel breaks up into interconnected fibrils as drawing proceeds. The relatively low number of tie molecules allows draw ratios of greater than 100 to be achieved without sample failure.

Keywords Polyolefin-gels; drawing; birefringence; X-ray patterns; orientation-processes; morphology

INTRODUCTION

Crystallization processes in polymer gels have been surveyed by Keller[1] and the gelation of dilute polyolefin solutions and its connection with the formation of surface grown fibres and the routes to ultra high modulus fibres have been reviewed recently[1–3]. The gelling network induced in the solution by stirring, or more precisely by local extensional flow fields, was thought to be the key feature controlling the subsequent morphology formed when the gel was drawn either wet or after removal of the solvent. The loose open structures of wet or dry gels allow very much higher extension ratios to be achieved on drawing gel fibres or films than can be attained with melt formed fibres or films[3]. Smith and Lemstra have achieved ultra high strength and modulus in fibres of polyethylene[4] produced by spinning solutions to gel filaments and subsequently drawing, and in drawn gel films of polyethylene[5]. They have shown that the maximum achievable draw ratio at 120°C varies inversely with the polymer concentration in the solution from which the gel was made[6].

Barham[7] has demonstrated very convincingly that the Pennings' type surface grown fibres and the ultra drawn gel films produced from high molecular weight polyethylene have the same basic structure deriving from the solution gelling network. Their tensile properties and maximum draw ratio/temperature curves were also virtually identical. From the stress–strain curves of swollen wet gels he derived the network characteristics. The drawn fibre mechanical properties were predicted on the basis of an aligned shish kebab model and were in good agreement with the measured data.

In this paper the changes in structural orientation associated with the ultra high draw ratio (> × 100) possible with gel material have been monitored by optical birefringence and wide angle X-ray diffraction.

EXPERIMENTAL

The high molecular weight polymers used were high density polyethylene HOSTALEN GUR 415 (ex Hoechst U.K. Ltd) and isotactic polypropylene HFO8 (ex ICI Ltd). The polymers were dissolved in hot solvent to form 0.5% or 1% w/v solutions in *p*-xylene or decalin. Temperatures close to the solvent boiling points were necessary to dissolve all polymer particles. The solutions were held under reflux and vigorous stirring with a PTFE coated magnetic stirrer was continued for about 15 min after optical clarity was observed. The hot solutions were transferred to an open beaker and stirred while cooling slowly to the gelation point around 90°C. In early experiments stirring was manual with a glass rod. Subsequently a four roll mill was preheated and immersed in the solution to create a more uniform extensional flow field[8]. The mill was constructed of 0.8 cm diameter rolls of 15 cm length with their axes of rotation at the corners of a 1 cm square. The rolls were made of stainless steel and the bearings made from polytetrafluoroethylene blocks and were unaffected by the hot solvents used. The mill was driven by a small d.c. electric motor fitted with a multi ratio reduction gear box and power was supplied through a variable speed control unit.

As soon as the increasingly viscous solution started to gel on slow cooling, indicated by build up of a gel layer on the rolls of the mill, stirring was stopped. The mill was quickly removed and the gel cooled to room temperature. The initially clear gels became turbid during this final cooling period.

The turbid gel then expelled some solvent by syneresis and shrank a little in volume. The syneresis was accelerated by applying unidirectional pressure[9] on the top surface of the gel and repeatedly decanting off the expelled solvent. Finally the gel slab was transferred from its container and pressed between filter papers in a laboratory hydraulic press at 77.5 MN m^{-2} load. The gel sheets, now one to three millimetres thick, still contained residual solvent and were stored without further change rolled up in the filter papers in screw top glass jars. Strips of the gel were then cut off the sheet, washed freer of residual solvent with acetone, and air dried. Infra-red spectra still showed detectable traces of the original gel solvent but this disappeared during the first stage of hot drawing to a low draw ratio.

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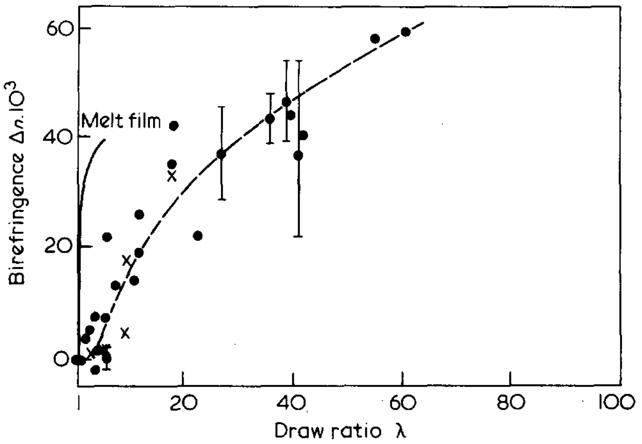

Figure 1 Variation of birefringence of GUR 415 gel films with draw ratio: —●— from 0.5% w/v decalin solutions; —X— from 1.0% w/v *p*-xylene solutions

The dry gel strips were clamped in a manual screw thread stretching frame which could extend a 1 cm long sample to up to 25 cm, i.e. a draw ratio of 25. Longer samples were used for lower draw ratios then halved in length and one half was redrawn to a higher ratio. In this way a series of drawn samples were made from a given supply gel sheet from × 1.5 up to × 100 draw down.

Isothermal drawing was achieved by immersing the whole frame in boiling water. Each sample was cooled to room temperature held to length. Space marks were put on the undrawn strip lightly with a ball-pen. If the sample drew down non uniformly through the formation and propagation of extended necks local effective draw ratios were calculated from the measured increase in length between marks.

Samples could be cold drawn by hand with difficulty but only to draw ratio of × 3 to × 6 to break. Often a multitude of sharp transverse necks formed and the strips always stress whitened. This internal stress failure could be healed by pressure from a stylus point or by cold rolling. The latter greatly reduced the energy loss by scatter and facilitated the recording of infra-red spectra. The shape of the scatter background of unrolled samples in the infra-red showed a broad transition with wavelength from reflection scatter to diffraction scatter over the range 5 to 10 μm suggesting that the stress whitening was caused by structural failures with spacings over this range of dimensions. The hot drawn samples showed very little stress marking by eye.

Samples were examined in a polarizing microscope for visual appearance with the film plane normal to the optic axis. Retardations were measured using a Babinet compensator. The fringe system of the Babinet is sensitive to local fluctuations in retardation across the width of the drawn specimen. The specimen thicknesses were measured with a metric micrometer screw gauge (0.01 mm per scale division, i.e. thicknesses estimated to 1 μm with the vernier) and their mean birefringences calculated (usually mean of six positions on drawn sample).

Wide angle X-ray diffraction patterns were recorded on a standard flat film camera with specimen to film distance of 3.5 cm using CuKα radiation. The patterns were recorded with the plane of the film samples mounted both flat on and edge on to the X-ray beam and the pattern of orientation changes with draw ratio were assessed by eye. Low angle X-ray patterns were recorded on a few samples using a Rigaku-Denki pinhole collimator vacuum camera with 40 cm specimen to film distance and a rotating anode high intensity source of CuKα radiation.

RESULTS

Optical microscopy

Both the polyethylene and polypropylene gel films exhibited the same pattern of drawing behaviour as observed between crossed polars with the draw direction at 45° to the polarizer/analyser axes.

The undrawn films exhibited no retardation colours but showed a weak retardation with no resolvable pattern and no detectable spherilitic structures. The stress whitening of the cold drawn samples made observation of retardation colours difficult except in the thinnest specimens but the appearance suggested parallel fibrils within the material of variable width within the range indicated by the infra-red scatter. In the hot drawn samples at low draw ratios fibrils of low retardation appeared within the material with their axes roughly parallel to the draw direction. With increased draw ratio each of these fibrils drew down apparently independently to develop strong uniform retardation colour along its length yet without the film losing lateral coherence. Drawn films could be fibrillated by lateral tension however. The draw down of each fibril was very apparent when a sharp neck formed and was viewed under the microscope. The overall appearance of the drawn films was of a multitude of parallel fibrils each of uniform colour along its length but the colours varying from fibril to fibril across the width of the film. This appearance was virtually identical to the surface grown films formed on a couette rotor reported previously[10]. This observation reinforces Barham's conclusion about the common origin of the morphology of these products[7].

The fringes in the Babinet Compensator used to measure the overall mean birefringence of the hot drawn films showed an ultrafine irregularity directly related to the parallel fibrils. The local fibril to fibril variation in retardation colour or Babinet fringe displacement probably arises as much from thickness fluctuations as from orientation differences between fibrils since it persists up to very high draw ratios when the X-ray patterns indicate high unit cell orientation.

BIREFRINGENCE MEASUREMENTS

GUR 415 polyethylene films

Results for the polyethylene films drawn at 100°C are plotted in *Figure 1* for gels from decalin and *p*-xylene. No significant difference due to solvent can be detected. At any draw ratio there is a film to film variation in birefringence as the scatter of mean values shows. Also in any one film at a given draw ratio there was a point to point variation in birefringence. The vertical bars indicate examples of the range of point to point values recorded at several draw ratios. The heterogeneous fibrillar structure of the films was probably responsible for this scatter of experimental results.

At low draw ratios, up to × 6 in some samples, the birefringence was low and fluctuated positive and negative over the area of the film. The birefringence then increases continuously with draw ratio and is still increasing with draw ratio at × 60.

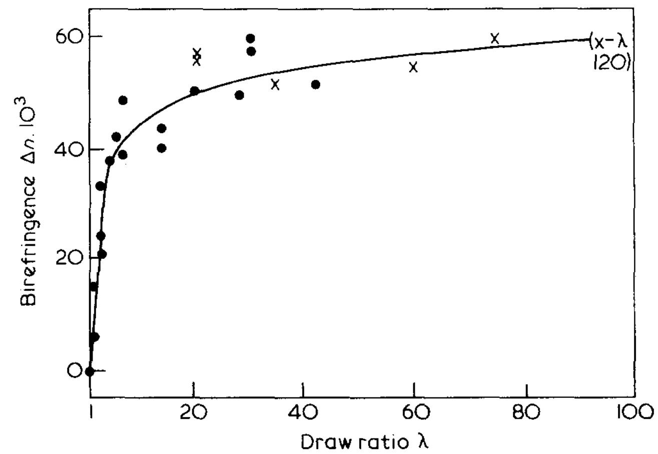

Figure 2 Variation of birefringence of GUR 412 gel films (ex Dutch State Mines) with draw ratio: —●— drawn at Bristol; –X– drawn at DSM Laboratory

GUR 412 polyethylene films ex Dutch State Mines Laboratory (*D.S.M.*)

Undrawn and drawn samples of gel films made from 1% decalin solution at D.S.M. were kindly supplied by Dr. Paul Smith for comparison. The birefringence results for their samples drawn at 120° or 130°C and their undrawn film drawn at 100°C in Bristol are collected in *Figure 2*. At 130°C they achieved a draw ratio of × 120 but although the maximum achievable draw ratio varies with drawing temperature[4c,7] the scatter in birefringence is much greater at any given draw ratio than any effect of drawing temperature.

Comparison of *Figures 1* and *2* shows that the birefringence develops faster with draw ratio in the D.S.M. gel films than in the Bristol preparations. No weak positive and negative birefringences were recorded at low draw ratios. Both differ from melt cast films (solid line in *Figure 1*—from ref. 11) which rise fast to a lower limiting birefringence at much lower ratios under normal drawing conditions.

Isotactic polypropylene

The birefringence-draw ratio curve for dried polypropylene gels from decalin solutions is given in *Figure 3*. These samples were all drawn at ~100°C. The dried films were more brittle than the polythene films and could not be cold drawn.

Initially at × 2 ratio the birefringence was negative and then became positive and increased continuously with draw ratio up to the maximum achieved draw of × 50 at break. The birefringence was not levelling off to a limiting value at this draw down however.

X-RAY DIFFRACTION RESULTS

GUR 415 polyethylene films

The dry undrawn films show no orientation with the X-ray beam normal to the flat surfaces of the sample. With the sample edge on to the horizontal X-ray beam and the flat surface of the sample in a vertical plane the diffraction pattern shows the (*hk*0) reflections arced on the meridian and the (*hkl*) reflections spread into arcs about the equator. This indicates a distribution of orientations about *c* axis normal to the sample plane and no other rotational constraints.

Low angle scattering recorded with the beam normal to the flat surface of the sample showed no detectable long spacing but very strong scatter around the back stop. With the sample edge on to the beam and the flat surfaces of the sample in a vertical plane the pattern showed strong sharp long spacing arcs on the equator. These two observations are consistent with chain folded crystalline lamellae oriented in the plane of the sample. The long spacing was 127 ± 2 Å. Clearly part at least of the crystallization occurring as the gel cools is by chain folding and the unidirectional pressure used to accelerate syneresis rotates the crystal lamellae as the gel is compressed.

A sample cold drawn × 5 showed no change in the wide angle X-ray orientations i.e. '*c*' axes still spread about the normal to the sample plane. The sample birefringence was -4.6×10^{-3}. The origin of this weak negative birefringence is not obvious since the wide angle X-ray pattern with beam normal to the sample showed no trace of any slight preferred unit cell orientation.

With a series of samples hot drawn to a range of draw ratios the orientation changes are more clearly exposed in the wide range X-ray patterns taken with the sample edge on to the beam: draw direction vertical. The orientation with *c* axis perpendicular to the film plane of the undrawn gel film progressively re-orients with increasing draw ratio. The (*hk*0) intensities, initially meridional arcs, split into short arcs either side of the meridian of the X-ray pattern and move towards the equator with increase in drawdown. As these reflections move around their intensity weakens and at the same time new (*hk*0) reflections appear and increase in intensity on the equator of the patterns. This suggests that as some of the chain folded lamellae tilt so that their *c* axes move towards the draw direction others break up (by shear?) and reform with *c* axes aligned in the draw direction.

These progressive changes are illustrated in *Table 1* where the *c* axis tilts were estimated from the positions of the (200) reflections.

The appearance of the (*hk*0) equatorial intensity between draw ratio 4 and 11.4 corresponds to the increase in birefringence. The WAXS patterns of the × 4, × 11.4 and × 22.8 samples are shown in *Figure 4* as an example.

The X-ray patterns taken with beam normal to the sample plane and draw direction vertical are consistent with the orientation pattern of *Table 1* but show less detail. As the *c* axes tilt towards the draw direction the (*hk*0)

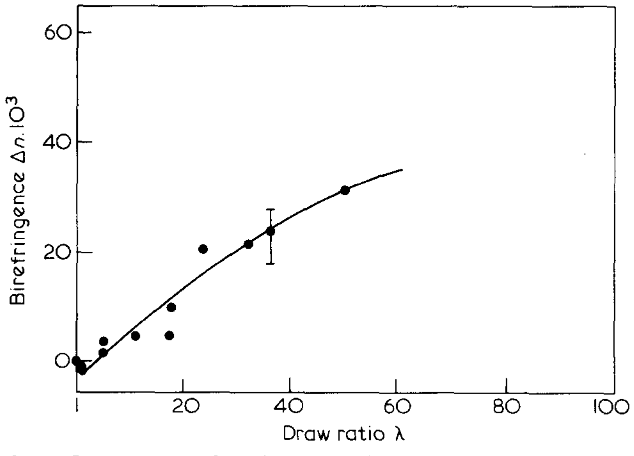

Figure 3 Variation of birefringence of polypropylene gel films with draw ratio

Table 1 **Comparison of orientation changes in edge on X-ray patterns with birefringence (GUR 415 gel from decalin)**

Draw ratio	1	4	11.4	22.8	41	Drawn to break
c axis tilts to draw direction	90°	±60°	±45° and 0°	±30° and 0°	±25° and 0°	0°
Birefringence		v. low	0.014	0.022	0.037	0.059

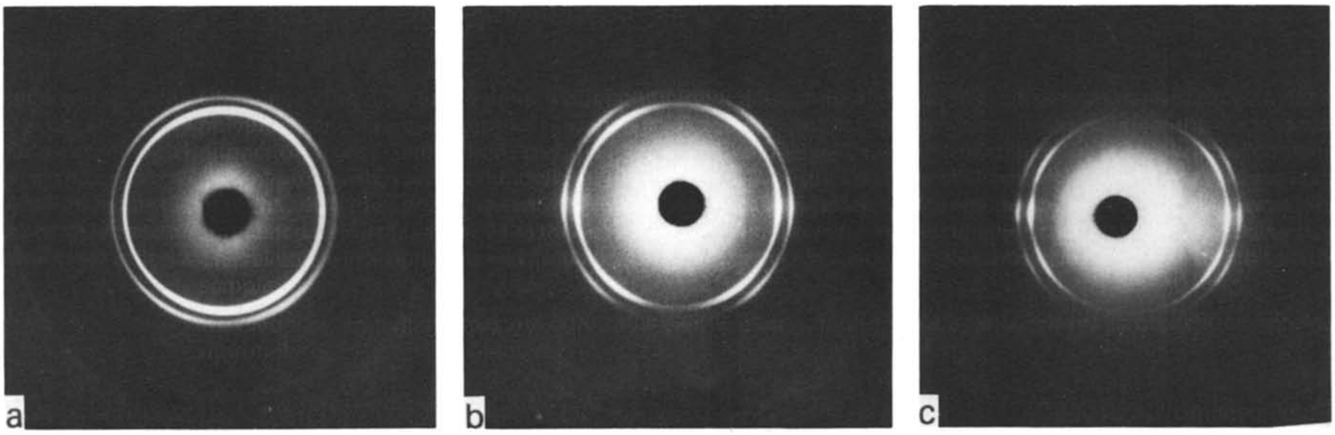

Figure 4 **X-ray patterns of drawn GUR 415 gel films. Draw direction vertical, X-ray beam parallel to film surface: (a) X4, (b) X11.4, (c) X22.8**

diffraction rings all contract slowly into arcs with maximum intensity on the equator while the (*hk*1) rings develop meridional arcs which shorten and move towards their final first layer line positions in the fully *c* axis oriented specimen at the highest draw ratio.

GUR 412 polythene films (ex D.S.M.)

A few X-ray patterns were taken of this series of samples. They showed analogous orientation behaviour with draw ratio to the GUR 415 gel films except that the '*c*' axis tilts occurred faster with draw ratio as the birefringence results anticipated (cf. *Figures 1* and *2*). For example, a sample of draw ratio × 1.5, Δn 0.015, showed *c* axes at ±60° in the 'edge-on' X-ray pattern with no *c* axes at 0° (cf. previous series, *Table 1*, × 4 draw ratio). Full *c* axis orientation in the draw direction was again achieved at the highest draw ratios.

Isotactic polypropylene films

Despite the slow development of birefringence with draw ratio of the polypropylene gel films similar to polyethylene their progression of X-ray orientation changes were very different. At all draw ratios including the undrawn film the patterns recorded with the X-ray beam normal to the sample plane were virtually identical to those with the beam edge on. The pressure applied to force syneresis thus produced no preferred orientation in the dried out gel films. The crystallization during cooling therefore does not develop any units whose shape would respond to pressure. This result was so surprising that a sample made in the laboratory press at 77.5 MN m^{-2} and kept with some solvent present was repressed at 620 MN m^{-2}. No preferred orientation was detected at this high pressure. Since high draw ratios were achieved the crystallized units must be as mobile as in polyethylene but roughly spherical in shape.

With increased draw ratio unoriented material remains present in the samples except at the highest draw ratio which caused a break (× 50). The proportion of unoriented material decreased progressively while the intensity of '*c*' axis parallel to draw direction reflections progressively increases: (*hk*0)'s on equator. Examples of the X-ray patterns for two draw ratios are given in *Figure 5*. Over intermediate draw ratios the (040) and (060) rings showed a slight intensity maximum on the meridian which indicates the presence of a small amount of material with *b* axis roughly parallel to the draw direction (*Figure 5a*). Even stronger '*b*' axis orientation was observed in earlier unpublished work by Lemstra, Acs and Keller, recently reported by Keller[1]. At higher draw ratios the innermost (110) ring showed a slight intensity maximum on the meridian when most of the crystalline material exhibited high *c* axis orientation (*Figure 5b*). Meridional intensity at the (110) position has been reported many times in the literature and assigned to an *a*-axis oriented material. However (130) reflections from *a*-axis oriented material, which should be as strong as (110), were not detected in the drawn gel films. (130) reflections are clearly seen in the X-ray patterns of melt spun polypropylene fibres (author—unpublished work). The reason for their absence in the gel films is not clear. The meridional reflections on the (110) unoriented ring are slightly split in *Figure 5b* due to a slight tilt of the sample as are the (022) reflections of the *c* axis oriented material. They are in the position of (011) reflections from *c* oriented material but these reflections are symmetry forbidden with the accepted space group and were absent in the pattern of the fully drawn (× 50) sample. Changes in space group between unoriented and fully oriented material have been suggested[12] but on balance the presence of a small amount of '*a*' axis oriented material at the middle draw ratios seems the more probable explanation.

The progression of these orientation changes is summarized in *Table 2* making very rough assessments of the relative amounts of unoriented material and '*c*' axis oriented material by eye based on the relative intensity of reflections.

DISCUSSION

Two major questions can be discussed on the basis of the experimental data presented above. Can the extremely high draw ratios achievable easily with dry polyolefin gels be understood more clearly in terms of the orientational changes? Can more detail of the gel morphology be deduced from the drawing experiments?

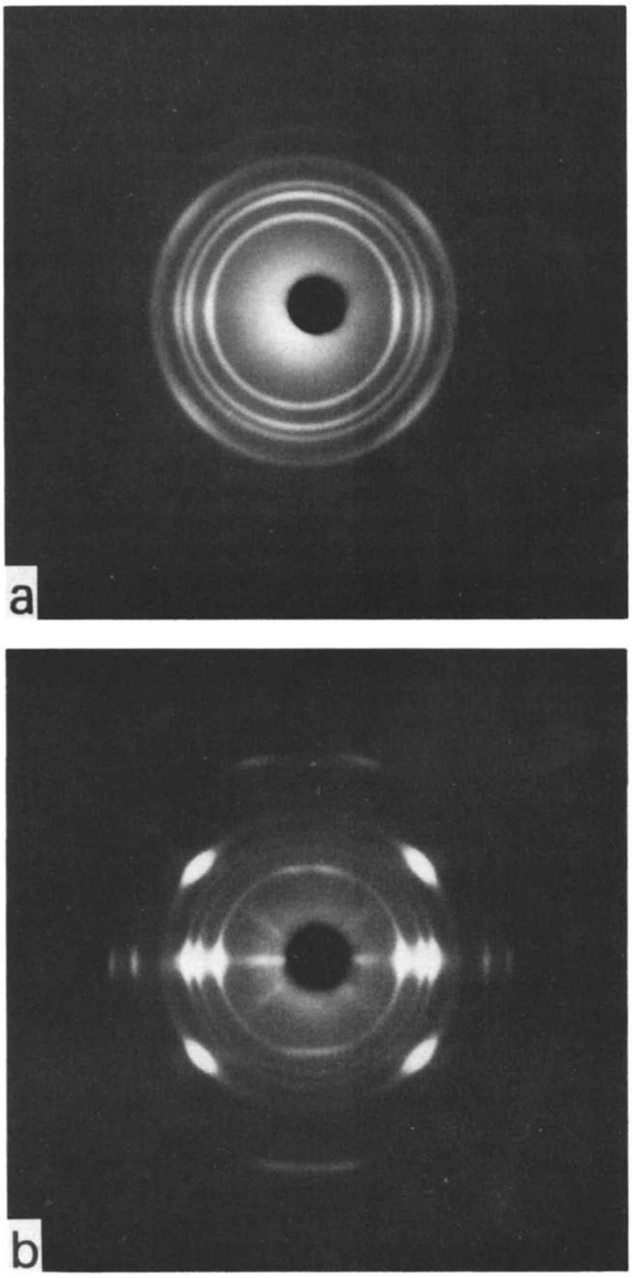

Figure 5 X-ray patterns of drawn polypropylene gel films. Draw direction vertical, X-ray beam normal to film surface: (a) X6, (b) X36

The propensity of the dilute polymer solutions to gel on cooling is much enhanced by stirring down to the gel temperature. Local extensional flow which is random with manual stirring or controlled using a four roll mill leads to chain extension i.e. a straightening of random coils. If segments of straightened chains aggregate into small bundle like crystals a gel network is created providing sufficient numbers of random coil chains linking the bundles[3,7].

This network once formed is thermally very stable since a gelled solution can be reheated to form a viscous liquid which gels again on cooling[10]. The viscous flow above the gel temperature and the optical clarity just below the gel point suggest that the crystalline regions forming the network junctions are very small and probably not very numerous. The bulk of the polymer chains then crystallize as the clear gel goes turbid.

For the polyethylene gels the X-ray data shows that this bulk crystallization process is predominantly the formation of chain folded lamellae. Their progressive re-orientation from *c* axis normal to sample plane in the pressed dry films as draw ratio increases suggests very strongly that the stretching of the gel network reorients the lamellae. This in turn suggests that some at least of those polymer chains incorporated in the network junction zones but not linking junction zones (cilia) are incorporated into the lamellae during the secondary crystallization, i.e. form loose tie molecules between the gel network and the chain folded lamellae. The numbers of tie molecules for lamella must be sufficiently small to allow the oriented lamellae to slip past each other in the cold drawing experiments where × 5 drawdown was achieved *without* change in lamella orientation. Yet the numbers of tie molecules must be sufficient to retain sample coherence despite the intense stress whitening observed on cold drawing.

Hot drawing allows the reorientation of lamellae at low draw ratios and facilitates break up of some of the lamellae to reform fully *c* axis oriented fibrils as drawing proceeds until all the material is '*c*' axis oriented at the highest draw ratios.

The initial partial fibrillation of the gel film at low draw ratios followed by apparently nearly independent draw down of the individual fibrils is possibly determined by the spacial distribution of the tie molecules; easiest slip occurring along the directions of lowest tie concentration. The fact that local areas of both weakly negative and weakly positive birefringence were observed in the same sample at very low draw ratios also reflects this micro-heterogeneity. The absence of negative birefringent areas and the more rapid re-orientation with draw ratio of the

Table 2 Comparison of orientation changes in X-ray patterns with birefringence (polypropylene gel from decalin)

Draw ratio	1	2	6	18	36	50
Unoriented	100%	100%	50%	25%	small	zero
'*c*' axis oriented	zero	trace	50%	75%	100%	100%
'*b*' axis oriented	zero	trace	weak	v. weak	v.v. weak	zero
(011)			trace	v. weak	weak	zero
Birefringence		–0.002	+0.002	+0.010	+0.024	0.032

Table 3 Some comparative birefringences for polyethylene samples. (All measured using the Babinet compensator)

Polyethylene – Normal drawn melt sample (x10)	0.040
Sedimented single crystal mats hot drawn (~x20) (supplied by Dr. P. J. Barham)	0.037 to 0.040
Gel film – hot drawn (x100)	0.060
Ultra high draw ratio highly fibrillated melt cast sample (ex P. J. Barham) (~x30)≃	0.080

Dutch State Mines laboratory product suggests that their gel preparation method or the different polymer used yields a less heterogeneous structure. Nevertheless the overall pattern of reorientation behaviour was the same as the samples prepared in our laboratory.

The results obtained for polypropylene are harder to interpret in detail since the morphology developed by secondary crystallization when the gel goes turbid showed no preferred orientation in the pressed dried film. Polypropylene exhibits a complex crystallography. Three unit cell symmetries are recognized, α, β and γ forms which can co-exist in the same sample[12]. Proportions vary with the method of sample crystallization.

Four different types of spherulite have been identified with either weak negative or weak positive birefringence[13].

When a chain folding morphology develops twinned intercrossing lamellae form in the elementary units which have their '*b*' unit cell axis common[14]. These units grow into into the final space filling structure as complex dendritic like aggregates.

The absence of preferred orientation in the highly pressed gel film suggests that the crystalline morphology is composed of iso-dimensional units approximating to spheres. Nevertheless, their break up and re-orientation on drawing suggests that, as in polyethylene, the gel forming network is linked by tie molecules to the secondary crystalline particles. A crystalline particle formed by aggregation of the twinned lamellae units with the common *b* axis radial would on deforming to an ellipsoid with long axis in the draw direction exhibit a weak '*b*' axis orientation as observed in the lower draw ratio samples. So also would the types I and II spherulites which have '*b*' axis tangential[14]. Before any significant break up of such ellipsoids to generate *c* axis oriented fibrils they would exhibit a weak negative birefringence (see *Table 2*). As soon as a significant amount of *c* axis oriented material is created by drawing the birefringence goes positive and the '*b*' axis oriented reflections weaken. The source of the weak meridional intensity on the (110) ring remains an open question but together with a more exact determination of the morphology associated with *b* axis oriented samples is being investigated by Dr. Mary Hill and Dr. W. S. Fulton in our laboratory.

The ultimate birefringence observed in the most highly drawn samples suggests a high perfection of orientation was achieved. Some comparisons are presented in *Table 3*.

The oriented micro fibrils both in the highly drawn gel films and in the ultra drawn melt sample could contribute form birefringence. A high draw ratio GUR gel sample was soaked for some days in immersion oil of refractive index 1.513 and its birefringence was lowered by 0.008 suggesting a small positive form birefringence.

A similar comparison between melt and gelled polypropylene is given below

$$\left.\begin{array}{lr} \text{Polypropylene drawn melt sample} & 0.034 \\ \text{annealed} & 0.027 \end{array}\right\} \text{(ref. 11)}$$

drawn gel extrapolated from *Figure 3*
~0.040

Because of the possible contribution of form birefringence, optical measurements alone are an uncertain guide to perfection of orientation.

The results obtained from sedimented crystal mats of polyethylene are of interest since they, like the undrawn gel films, have *c* axis normal to the sample plane. As *Table 3* shows, they can be drawn about ×20 to break with 0.040 birefringence, whereas the gel films, probably because of the extra coherence provided by the gel network can be drawn much further to a higher birefringence.

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