polymer papers

The morphology of highly drawn polyoxymethylene and evidence for a temperature dependent crystal modulus

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Measurements of the crystalline modulus of highly oriented polyoxymethylene have been undertaken for a range of different samples over the temperature range from −150°C to 50°C. The crystalline modulus measurements have been combined with measurements of mechanical modulus, and X-ray structural measurements. A consistent interpretation of all the results has been given in terms of a three phase model in which an oriented amorphous phase acts in parallel with a parallel lamellar structure of crystalline and amorphous phases in series. Clear evidence for the temperature dependence of the crystalline modulus has been obtained from highly annealed samples which show the simpler two phase parallel lamellar structure.

(Keywords: polyoxymethylene; morphology; crystal modulus; X-ray analysis)

INTRODUCTION

In a previous publication[1] we reported some preliminary dynamic mechanical and crystal–strain measurements on ultra high modulus oriented polyoxymethylene (POM). A result of particular interest was the comparison of the longitudinal elastic modulus of the crystalline regions, deduced from X-ray studies of oriented tapes under stress, with the low temperature dynamic Young's modulus. The greatest observed value for this dynamic Young's modulus exceeded the value of the crystal modulus which had previously been reported by Sakurada *et al.*[2] and therefore cast some doubt on the validity of that value.

In this paper we report upon a more extensive series of measurements and suggest a model for the morphology of oriented POM which has, as one of its features, a crystalline modulus which varies with temperature. Results will be presented and discussed for the variation with temperature of both the apparent crystal modulus, determined from the X-ray measurements under stress, and the mechanical Young's modulus, in a wide range of oriented samples. We conclude that the structure of highly drawn POM is markedly different from the structure of highly drawn polyethylene (LPE), in which quite a simple model (the crystalline bridge model[3]) was able to account satisfactorily both for the variation of Young's modulus with draw ratio[3] and for the way in which the apparent crystal modulus varies with temperature[4].

We see no evidence for crystalline bridges as suggested by Choy *et al.*[5] Also, these authors do not consider a temperature dependent intrinsic modulus the evidence for which is quite strong in our work. Biswas and Sengupta[6] propose a two phase model for drawn POM whereas we consider a three phase model to be nearer reality. Few, if any, polymers can be modelled by only two phases and this is especially true for POM since it does not crystallize easily and there is a strong likelihood that a drawn sample will contain much aligned but not ordered material.

EXPERIMENTAL

Sample preparation

Highly drawn narrow tapes were prepared following the procedures described by Brew and Ward in a previous publication[7]. The starting material was a commercial grade of POM (Delrin 500, kindly supplied by E. I. du Pont de Nemours, Ltd) which has a weight average molecular weight of about 90000. Isotropic sheets were prepared by compression moulding pellets in a hot press at 200°C, at a pressure of 1 MPa for 4 min, followed by rapid quenching into water at ambient temperature.

Dumbbell samples cut from these sheets were drawn in an Instron tensile testing machine at 145°C at crosshead speeds of 1 cm/min and 10 cm/min to draw ratios between 9 and 21. Samples drawn at 1 cm/min to draw ratios of 8.0 and 20.6 were also annealed at constant length in a vacuum oven for 24 h at 165°C.

Mechanical characterization

The Young's modulus of each sample was measured in a standard dead loading creep apparatus over a range of temperatures down to −150°C and there was good agreement with the figures measured for similar samples by Brew and Ward[7]. The values quoted refer to the secant modulus calculated from the 10 s isochronal stress–strain curves at a strain of 10^{-3}. The cross-sectional areas of the samples were estimated by weighing a length of sample in a microbalance and determining the sample densities.

Density measurements were made on each sample using two different techniques. Straightforward mensuration gave an overall density which was then compared with the density found in a carbon tetrachloride–toluene graduated density column. A void fraction was determined from the two figures. A check on the results was carried out by determining the mass per unit area of the tape specimen by measuring the attenuation of a monochromatic X-ray beam passing

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through normal to the plane of the tape. Multiplying by the density gave an effective thickness which was compared with the measured thickness to give the void fraction. An assumption is made, when this technique is used, that the attenuation of the beam is uniform over the area of sample exposed to the beam. Providing there are no gross inhomogeneities such as giant voids this is a reasonable assumption and there was no evidence of such voids from either optical or electron microscopy. The fact that the void fractions so determined were in sensible agreement with those determined by mensuration gives added confidence that the measurements were reliable.

X-ray and microstructure measurements

A Siemens scanning diffractometer was used to measure (a) accurate profiles of X-ray reflections and (b) changes in Bragg angle occurring upon mechanically straining the samples.

The profiles were measured by operating the diffractometer at high resolution (*ca.* 0.1° in 2θ), using a step scanner to record the experimental profile, and then deconvoluting the observed profile and the instrumental profile using a standard Stokes technique[8]. The instrumental profile was measured from a metallic sample with the same geometry as the polymer sample utilising a reflection whose Bragg angle was as close as possible to the one whose profile was desired.

Changes in Bragg angle, as the samples were strained, were recorded using our previously reported technique[4]. Briefly, the fibres were held in a horizontal extensometer to which a dead load could be applied, and which was mounted on the diffractometer turntable. The profile of the chosen reflection was recorded for a number of loads and its centroid then determined by fitting a smooth curve to the data points. The computer program which carried out the latter operation fitted a combination of a background, a Gaussian curve and a Lorentzian curve and the centroid was taken to be the centroid of the latter two curves (which coincided). This procedure was found to be more reliable for POM than the simpler 'two point counting technique' which was used successfully on LPE[4]. The reasons for this are a little obscure but the most likely explanation is that the POM profile changes shape during the straining process and this invalidates the simpler technique. It is to be noted that strain crystallization can occur in POM and this will certainly alter the line profile.

Measurements were made from room temperature down to -165°C by immersing the sample in a temperature-controlled stream of nitrogen gas. The quantity deduced from the measurements was the apparent lattice modulus, i.e. the overall applied stress divided by the calculated lattice strain.

Larger scale density fluctuations in the sample were investigated using a small angle X-ray camera (after the design of Franks[9] manufactured by Searle Instruments Ltd). The photographic record provided enabled lamellar spacings to be deduced and indicated the presence of fibrillation in the samples over a scale of some tens to about 200 Å.

A Stereoscan 600 scanning electron microscope was used to investigate the microscope structure of the fibres. The microscope was operated at 7.5 kV and magnifications of around 3000 were used.

RESULTS

Young's modulus

A number of samples of different draw ratio and draw speed were investigated. Full results are to be found in ref. 11. The results were consistent with previous work[1] and confirmed that the highest figure measured is comparable with the lattice modulus value of 54 GPa proposed by Sakurada *et al.*[2]. An interesting feature was the dependence of mechanical properties on drawing speed. This contrasts with experience in linear polyethylene[10], where, provided that an optimum draw temperature is selected, the Young's modulus depends only on the draw ratio. This result for POM is indicative of the fact that there are significant differences in the deformation processes occurring during drawing. One should therefore perhaps not be too surprised if the morphology of drawn POM is different from that of drawn LPE.

Density and void fraction

A set of figures for the samples drawn at 1 cm min^{-1} is shown in *Table 1*. It will be seen that there is no obvious trend with draw ratio and the conclusion that we draw is that a void fraction of some 14% is common to all samples. Specimens drawn at the higher speed of 10 cm min^{-1} show a set of figures of similar nature with an identical average void fraction.

A proportion of the voids occur because of the fibrillation which takes place during the drawing process. This phenomenon is well seen in the scanning electron microscope (SEM) photographs of which a typical example is seen in *Figure 1*.

Crystallite size

Diffraction peak profiles were measured for two meridional reflections (009) and (00 18) and an equatorial reflection (100). From the integral breadths of the

Table 1 Void fractions in POM samples drawn at 1 cm min^{-1}

Draw ratio	Density from mensuration (g cm^{-3})	Density from density column (g cm^{-3})	Void fraction (%)	Thickness from mensuration (mm)	Thickness from X-rays (mm)	Void fraction (%)
9.2	1.17±0.07	1.412±0.002	21±7	0.265±0.005	0.225±0.001	18±2
11.5	1.30	1.417	9	0.245	0.219	12
12.2	1.23	1.422	16	0.230	0.211	9
15.0	1.31	1.416	8	0.210	0.181	16
18.5	1.21	1.408	16	0.215	0.190	13
20.6	1.21	1.414	17	0.190	0.164	16

reflections ($\Delta(2\theta)$) a figure for the mean crystallite size was deduced using the Scherrer equation

$$\bar{L}=k\lambda/\Delta(2\theta)\cos\theta$$

with k taken as unity (Stokes and Wilson[8]).

The results appear in *Tables 2* and *3* where values of $\bar{L}$ are calculated from integral breadths which have been corrected for the Lorentz-polarization factor and the variation of the unit cell structure factor across the profile. Differences between the L values of the two meridional reflections will be noted and these are accounted for by the fact the width of the line arises both from finite crystallite size and from lattice disorder. The availability of two orders of reflection in the meridian enables these two effects to be separated and a better approximation to the crystallite size determined. The procedure for carrying out this exercise is described in detail by Jungnitz[11] but is, briefly, as follows.

The observed integral breadth of the reflection is given by

$$(B_{\text{observed}})^2=(B_{\text{finite size}})^2+(B_{\text{disorder}})^2$$

The first term on the right hand side is given by the Scherrer equation

$$B_{\text{finite size}}=\frac{\lambda}{\bar{L}\cos\theta}$$

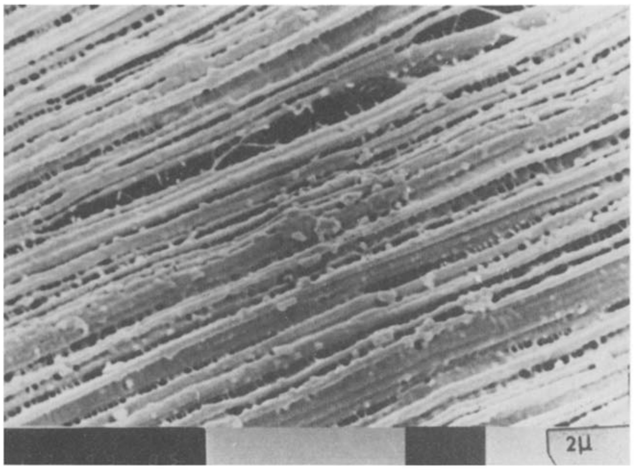

Figure 1 An electron micrograph of a sample of POM tape drawn to a draw ratio of 18.8:1 at a speed of 10 cm min^{-1}

The effect of disorder has been treated by many authors (e.g. Warren and Averbach[12]) and the outcome of a typical analysis is that

$$B_{\text{disorder}}=\frac{\pi^2 l^2 g^2}{d}$$

where l is the order of the reflection, g is a disorder parameter and d is the appropriate lattice spacing. Since we have two reflections available the effect of the disorder can be separated, for the chain direction, and a realistic mean size determined. The procedure was not possible for the equatorial reflection since only the (100) reflection was seen with sufficient intensity for its profile to be measured accurately.

The results of the separation procedure are seen in the fifth column in *Table 2* and indicate that there is substantial disorder present in the POM crystal lattice in highly drawn specimens.

The general deductions that can be made from the figures in *Table 2* are that the mean crystallite size in the draw direction increases as the draw ratio increases but does not, with one exception, exceed (within the experimental errors) the long period as determined by small-angle scattering (see below). This behaviour is in sharp contrast to the situation with highly drawn polyethylene in which mean crystallite sizes exceed by more than a factor of two the lamellar long period. We thus suspect immediately that the ordered crystal bridge model proposed for polyethylene is unlikely to hold for POM and that long range order is not preserved through more than one lamellar unit.

Lateral crystallite sizes are shown in *Table 3* and,

Table 3 Equatorial crystal sizes (perpendicular to draw direction)

Draw speed	Draw ratio	Crystal size $\bar{L}$ (Å)
1 cm/min	8	114±5
	12.2	100±4
	14.6	110±4
	18.5	111±4
	20.6	120±5
10 cm/min	9	103±4
	16	120±5
	18.8	104±4
Annealed samples		
1 cm/min	8	156±6
	20.6	144±6

Table 2 Meridional crystal sizes (draw direction)

Draw speed	Draw ratio	$L_{(0\,0\,9)}$ (Å)	$L_{(0\,0\,18)}$ (Å)	$\bar{L}$ (Å)	$g\times10^3$
1 cm/min	8	126±5	92±4	130±6	6.4±0.3
	12.2	152±6	94±4	162±8	6.9±0.3
	14.6	173±7	98±4	186±9	6.9±0.3
	18.5	173±7	97±4	188±9	6.9±0.3
	20.6	186±7	95±4	206±10	7.2±0.4
10 cm/min	9	134±6	81±3	143±7	7.5±0.4
	14.2	150±6	83±3	163±8	7.5±0.4
	15	146±6	80±3	160±8	7.8±0.4
	16	157±6	87±3	172±9	7.3±0.4
	18.8	161±6	81±3	180±9	7.8±0.4
Annealed samples					
1 cm/min	8	147±6	96±3	154±6	6.7±0.3
	20.6	210±8	97±3	241±8	7.2±0.4

although the absolute values are not reliable since disorder effects could not be separated, the general trend is that they remain constant throughout the drawing process.

Lattice strain

The lattice strain measurements give us a figure which we call the apparent lattice modulus and *Figure 2* shows the variation in this quantity with temperature for two different specimens. *Figure 3* shows the same variation for the annealed specimens. The general pattern is similar to that reported previously for a single specimen but the more comprehensive set of data here enable us to develop a model for the morphology of the material.

Small-angle X-ray measurements

Small-angle X-ray photographs were taken for the undrawn material and for two different draw ratios drawn both at 1 cm min^{-1} and 10 cm min^{-1}. There is evidence in all the photographs of lamellar structure with a long period of 190±10 Å although the more highly drawn specimens show very much weaker scattering from the lamellae than do the others. Conversely the high draw ratio samples exhibit strong equatorial streaks indicating the existence of considerable non-correlated density fluctuations across the fibres which are smaller in scale by a factor of a hundred or so than the fibrils evident in the SEM photographs.

The 'lamellae' reflections were generally not simple two bar patterns, which are characteristic of simple parallel lamellae, but showed evidence of a four point pattern which arises from a chevron structure. The chevron structure is not strongly developed however and probably indicates a sheared and deformed parallel lamellae texture.

It should be noted that the ascription of a 'Long Period' to the morphology of our samples is based upon simple small-angle X-ray diffraction patterns containing only one intensity maximum. Although this process is not entirely without ambiguity it is generally regarded as a reasonable thing to do since in specimens of, for example, drawn polyethylene, which have a very well developed lamellar structure, long exposures show the existence of a second order maximum which gives a long period identical with that deduced from the first order alone. We consider therefore that the Bragg equation can be used with some confidence to give information about the existence of periodic structure at the 100 Å level when we only have available a simple diffraction pattern.

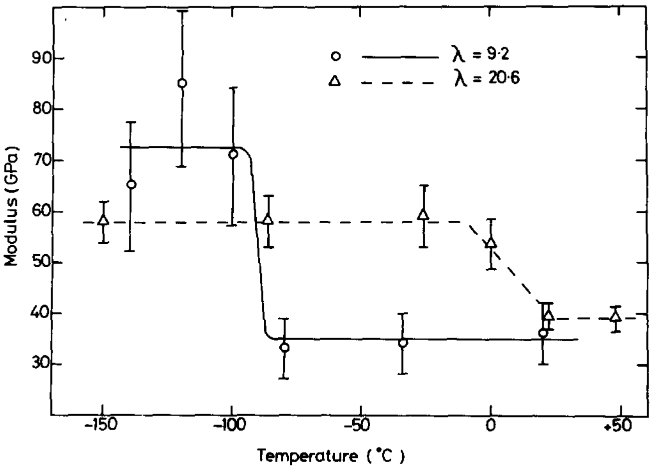

Figure 2 Variation with temperature of the apparent crystalline modulus of two 'as drawn' POM tapes of different draw ratios

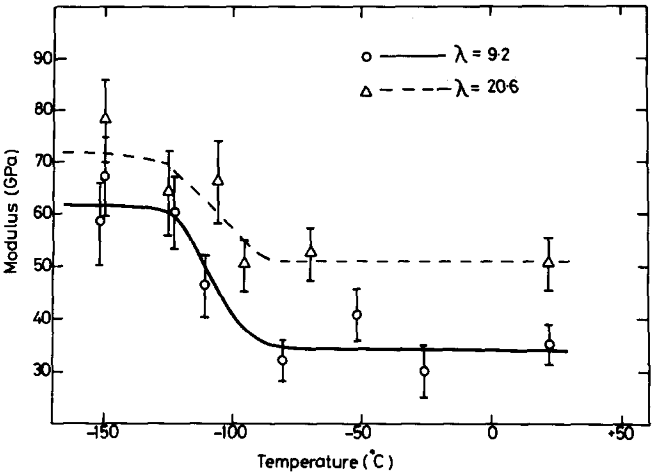

Figure 3 Variation with temperature of the apparent crystalline modulus of two annealed POM tapes of different draw ratios

DISCUSSION

General features of mechanical behaviour and crystal strain measurements

The features of the measured properties of the oriented POM tapes which are germane to the establishment of a morphological model which will provide an understanding of both the mechanical behaviour and the crystal strain measurements are as follows:

(1) The Young's modulus depends on the draw rate as well as the draw ratio. It varies with temperature, and the maximum value measured for the highest draw specimens is about 60 GPa, somewhat greater than the crystal modulus proposed by Sakurada *et al.* from their X-ray measurements of crystal strain.

(2) A two-point (or four point) small-angle pattern is seen in all samples, although it is very weak in the highest draw materials. This pattern is considered to indicate the presence of a lamellar texture. The long period spacing remains constant from specimen to specimen at about 190 Å, consistent with the choice of constant draw temperature.

(3) The mean crystallite length in the '*c*' direction (chain axis direction) is, after correcting for disorder, nearly always less than (or in the highest draw sample, approximately equal to) the long period.

(4) The apparent lattice modulus varies markedly with temperature, exhibiting the greatest values at low temperatures. The temperature region where the rise occurs varies from specimen to specimen and is greater for higher draw specimens, in contrast to the behaviour seen in LPE[4].

(5) The low temperature (−160°C) plateau value of the apparent lattice modulus varies from specimen to specimen, again in contrast to the situation with highly drawn LPE. Note especially the very clear results for two

annealed drawn samples (*Figure 3*) in which the 'limiting' crystal moduli differ from one another and also vary with temperature.

The above information, in conjunction with details of the variation of Young's modulus with temperature, provides a basis upon which models of the highly oriented POM tapes, either with or without an annealing treatment, can be built up.

The difference seen between POM and LPE lead us to search from the outset for a model which differs from the crystalline bridge model which was proposed for the latter.

Preliminary attempts at models for observed behaviour

Full details of the initial search for a model are to be found in ref. 11, in which two and three component Takayanagi models are explored in detail. We will only indicate the principal lines of argument here.

A simple series model with the crystalline and amorphous regions in series predicts a constant apparent crystal modulus equal to the true crystal modulus. In a simple parallel model the crystal strain is identical to the macroscopic strain and the apparent crystal modulus equals the macroscopic modulus. It can be seen that the predictions of both the simple series and parallel models are not correct.

Next, the Takayanagi models (either Series–Parallel or Parallel–Series) with the crystal phase as the continuous phase were considered. There is clearly no support for this type of model from the X-ray measurements (crystallite lengths do not significantly exceed the long period) and it predicts that the rises in apparent crystal modulus should occur at lower temperatures for higher draw samples, which is contrary to the results.

Finally Series–Parallel or Parallel–Series models with a new third phase, an oriented amorphous phase, were examined. This third component is considered to be a phase intermediate between that of the fully ordered crystalline state and the disordered or amorphous state. This model does appear to be more realistic than any of the previous model in terms of the structural information available. The effect of draw rate on the final modulus has been taken to indicate that the orientation of the amorphous regions as well as motion of chains through the crystal is essential to optimum drawing of POM. However, it was found that although the mechanical modulus could be modelled, it was not possible to reproduce the observed pattern of behaviour in the apparent crystal modulus with physically meaningful changes in the modulus of either this intermediate phase or the other amorphous phase.

At this juncture it would be possible to introduce more components into Takayanagi-type models in an attempt to simulate the observed behaviour. It was, however, considered to be more realistic to look for some basic physical fact or phenomenon which had been overlooked.

Evidence for a temperature-dependent crystal modulus

Attention was given to the actual elastic modulus of the crystal lattice which has so far been assumed to remain constant as the temperature is varied. We will consider first the experimental evidence for a temperature-dependent crystal modulus, and secondly related structural studies which support this idea.

In our previous studies of polyethylene it was shown that when a low draw ratio sample was annealed at high temperatures, the apparent lattice modulus was independent of temperature and had a value equal to the low temperature value seen in all unannealed specimens[4]. For such samples there is excellent structural evidence from X-ray diffraction measurements (comparison of crystal length with long period) and nitric acid etching followed by gel permeation chromatography[13], that the structure consists of alternating blocks of crystalline and non-crystalline material, i.e. a simple two phase series model. Hence in all cases the crystal strain measurements determine the true lattice modulus.

We suggest that the annealed POM samples also have a morphology which can be approximated to by assuming a simple two phase series model. Good evidence for this assumption is obtained from the similarity of values obtained for the crystalline fraction by two independent methods: (a) a comparison of the long period and the mean axial crystal thickness (b) and the true density of the specimens as measured in the flotation column.

All samples show the same long period of 190 ± 10 Å. The annealed specimen of draw ratio 8 had a measured crystal thickness of 154 ± 6 Å corresponding to a crystalline fraction of 0.81 ± 0.05. The density of the specimen was found to be 1.4305 g cm^{-3}. Now from the dimensions of the unit cell[6] we know that the density of crystalline POM is 1.49 g cm^{-3} and the density of amorphous POM has been given as 1.25 g cm^{-1}. From these figures we calculate a crystalline fraction of 0.75 which is in good agreement with the figure found above. The suggestion of a simple series model is thus quite strong.

The annealed specimen of draw ratio 20.6 shows different properties. There is little or no SAXS evidence of lamellar structure and the mean crystal thickness is slightly greater than the long period measured in the other samples. The similarity between the two curves of *Figure 3* suggests however that the low and high draw ratio samples are similar to one another and we assume that they both have a series structure which is not quite as well developed in the low draw specimen as in the high draw samples. There is thus some measure of stress concentration in the low draw sample leading to a slightly reduced apparent lattice modulus.

We take it therefore that the true lattice modulus is represented by the upper curve of *Figure 3*. The next step is to look for corroborating evidence of a variable intrinsic lattice modulus. Calculations of the lattice modulus of POM have led to quite widely varying values which have borne little relation to any measured values. The principal reason for this is that the molecule takes up a helical conformation when it crystallizes which introduces additional constraints upon its ability to deform freely when the crystal lattice is strained. Asahina and Enomoto[14] give figures for the modulus of 150 GPa or 220 GPa depending upon whether the rotation angle of the chains remains fixed or whether extension takes place only through changes in the rotation angle. On the other hand, Sugeta and Miyazawa[15], using a method developed specifically to cope with helical chains, suggested that the modulus should lie between 40 and 95 GPa depending upon whether the chain was allowed to rotate freely during deformation or whether it could not rotate at all. These figures were for the 9/5 helical conformation which the chain takes in the more common trigonal crystalline form. If they took the case of the orthorhombic crystal, for which the chain takes a 2/1 helical conformation, then the calculated moduli fell to 19 and 48 GPa respectively. Clearly freedom to rotate is of key importance in establishing the actual value of the crystalline modulus and one could well imagine a situation where an imperfect crystal might exhibit a behaviour intermediate between the two extremes contemplated by the latter authors.

Next we consider the thermal motion of the molecule as has been investigated for example using n.m.r. and X-ray techniques. A number of workers[16–18] have investigated POM and have found that the chains show a substantial degree of motion both vibratory—along the chain axis—and rotational—around the axis, at room temperature. Amplitudes of the latter have been quoted as of order 30° and, what is more important, the motion is found to be strongly temperature dependent and effectively vanishes at around −120°C.

Now when a perfect crystal is homogeneously deformed the component chains cannot, in principle, rotate. However, if there is some thermal motion, then the lattice can be thought of as being 'loosened' and allowing a small degree of steady rotation of the chains when the whole structure is strained. We suggest therefore that the fall in apparent lattice modulus which is seen in the specimens considered above, as the temperature is increased, reflects a change in the actual modulus which arises from this effect.

Modelling of drawn POM fibres

The low draw ratio tapes show mechanical properties which are not very different from the low draw annealed tapes and we propose that they may be modelled in the same way, i.e. by a two phase series system. The high draw ratio tapes require a more complex model and we propose a three phase system as shown schematically in *Figure 4*. Two of the phases are conventional crystalline and disordered material but the third phase consists of chains which are generally aligned in the draw direction, packed tightly enough to introduce some (temperature dependent) constraint upon their ability to stretch when the fibre is stretched but not packed in crystalline register. Peterlin[19,20] and Prevorsek[21] have discussed the possibility of the unravelling of chains in lamellae during drawing and the outcome of this will, of course, be aligned, disordered chains. Now in an easily crystallizable substance such as polyethylene any such unravelled chains can fairly easily re-order leading to regions of crystallinity of increased length, i.e. we have the crystal bridge model to which earlier reference has been made. However, POM crystallizes far less easily owing to the more complex, helical, form of the lattice and it is reasonable to suppose that the unravelled molecules will remain aligned and taut[20] but not laterally ordered. In this state they will of course contribute significantly to the strength of the fibre but, being free to rotate, not to such an extent as if they were ordered.

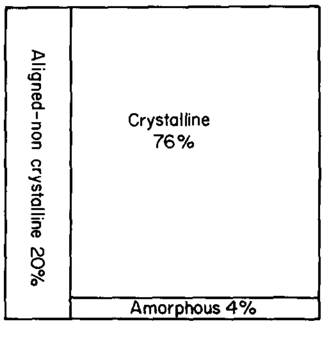

Figure 4 Schematic structure for POM tape drawn to a draw ratio of 20.6:1

The void fraction has not been included in these calculations since there is no obvious location for it. The general effect could be to introduce an uncertainty in the absolute values of the elastic moduli but the general picture of the structure that we propose will not be altered.

In attempting to model our samples using such a complex system it will be appreciated that there are many disposable parameters and any combination which is successful is highly unlikely to be unique. We do not therefore claim to provide a definitive structure but one which is realistic in its general outline. The procedure that we have adopted is to assume a structure for the highest draw specimen and choose elastic moduli for the three phases which either follow from our own experiments, as in the case of the crystalline modulus, or which enable us to predict the way in which the Young's modulus and the apparent crystalline modulus of the fibre vary with temperature.

Figure 5 shows the assumed variation with temperature of the elastic modulus of each of the three phases. The crystalline modulus used was the measured apparent modulus for the high draw annealed specimen. The modulus of the third phase was allowed to vary between the limits suggested by Sugeta and Miyazawa for 'free' chains in the 2/1 helical conformation. The lower limit, with freedom to rotate, obtains at room temperature and the higher limit, with the freedom to rotate lost, at the lowest temperatures. The detailed variation was chosen to optimize the modelling. A smoothly ranging amorphous modulus was also assumed. There are no experimental data for the amorphous modulus so we had to make a reasonable estimate of some plausible figures.

The experimental and assumed data were then inserted into the conventional Takayanagi series parallel model and values for Young's modulus and apparent modulus calculated.

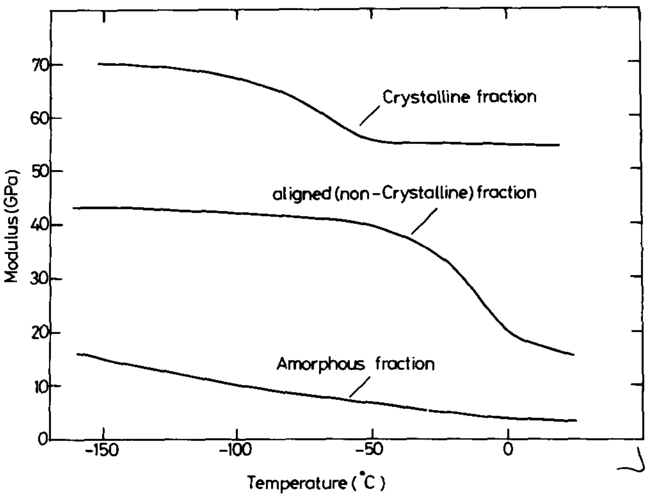

Figure 5 Variation with temperature of the Young's modulus of the three different phases present in a highly drawn POM tape

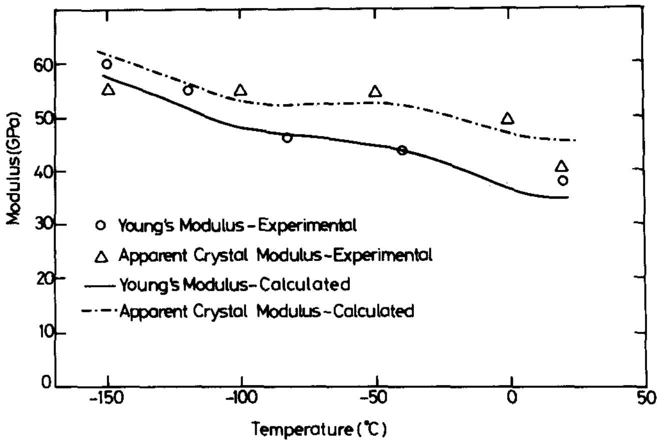

Figure 6 Comparison between the calculated and measured moduli for POM tapes of draw ratio 20.6:1

Figure 6 shows the comparison between experimental values for the apparent crystal modulus and those calculated using the model and, bearing in mind the difficulty of modelling such a complex system, the comparison is really quite good.

CONCLUSION

The important feature of this work is that we have demonstrated that the intrinsic Young's modulus in the chain direction of crystalline POM is temperature dependent. The models that we suggest for highly drawn fibres include a third component which also has a temperature dependent modulus. We do not claim that the detailed modelling is definitive but we are confident that the general features of the morphology are as described and that the differences which exist between POM and its less complex cousin, polyethylene, arise from the differences between the crystalline structures. PE crystallizes easily and when the crystal is deformed in the chain direction the planar zig zag simply straightens out a little. The helical conformation of the POM chain in the crystalline lattice makes it more difficult for aligned chains to come into crystalline register and the fact that the coiled molecule has to undergo rotation when the lattice is strained leads to a temperature dependent behaviour which is reflected both in the variation of the mechanical modulus with temperature and in the variation of the apparent crystalline modulus with temperature.

REFERENCES

1 Brew, B., Clements, J., Davies, G. R., Jakeways, R. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 351
2 Sakurada, I., Ito, T. and Nakamae, K. *J. Polym. Sci., C* 1966, **15**, 75
3 Gibson, A. G., Davies, G. R. and Ward, I. M. *Polymer* 1978, **19**, 683
4 Clements, J., Jakeways, R. and Ward, I. M. *Polymer* 1978, **19**, 639
5 Choy, C. L., Leung, W. P. and Huang, C. W. *Polym. Eng. Sci.* 1983, **23**, 910
6 Biswas, P. K. and Sengupta, S. *Makromol. Chem. Rapid Commun.* 1984, **5**, 295
7 Brew, B. and Ward, I. M. *Polymer* 1978, **19**, 1338
8 Stokes, A. R. and Wilson, J. C. *Proc. Camb. Phil. Soc.* 1942, **38**, 313
9 Franks, A. *Proc. Phys. Soc. (London)* 1955, **B68**, 1054
10 Capaccio, G., Crompton, T. A. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1641
11 Jungnitz, S. PhD. Thesis, University of Leeds, 1982
12 Warren, B. E. and Averbach, B. L. *J. Appl. Phys.* 1952, **23**, 497
13 Ward, I. M. and Williams, T. *J. Macromol. Sci.* 1971, **B5**, 693
14 Asakina, M. and Enomoto, S. *J. Polym. Sci.* 1962, **59**, 101
15 Sugeta, H. and Miyazawa, T. *Polym. J.* 1970, **1**, 226
16 Chiba, A., Hasegawa, A., Hikichi, K. and Furuichi, J. *J. Phys. Soc. Jpn.* 1966, **21**, 1777
17 Olf, H. G. and Peterlin, A. *J. Appl. Phys.* 1964, **35**, 3108
18 Shibita, T. and Iwayanagi, S. *Polym. J.* 1978, **10**, 599
19 Peterlin, A. *J. Polym. Sci., C* 1963, **9**, 61; 1967, **15**, 427; 1967, **18I**, 123
20 Peterlin, A. *J. Mater. Sci.* 1971, **6**, 490
21 Prevorzek, D. C. *et al. J. Macromol. Sci., Phys.* 1973, **B8**, 142