Investigation of the properties of directionally solidified poly(vinylidene fluoride)*

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Zone solidification at low growth rates succeeded in producing large films of oriented α-PVF$_2$ spherulites. The other polymorphs were either absent or unoriented due to their rapid encirclement by the much faster growing α-form. The high anisotropy of our samples was confirmed by optical microscopy, X-ray diffraction and polarized infra-red spectroscopy. It was found that unit cell orientation in spherulites of α-PVF$_2$ is such that the *b*-axis is radial. Dynamic mechanical behaviour of films both along the direction of solidification (longitudinally) and normal to it (transversely) is in qualitative agreement with a two-phase model proposed by Takayanagi. The behaviour of isothermally crystallized samples approaches that of longitudinal sections at high temperatures and that of transverse sections at low temperatures. Piezoelectric response of zone solified α-PVF$_2$ poled at low fields is similar to that of a random α-spherulitic sample and almost two orders of magnitude lower than that of a uniaxially drawn film.

INTRODUCTION

Poly(vinylidene fluoride) (PVF$_2$ or PVDF) has received wide attention during the past decade, mostly as a result of its piezoelectric properties[1,2]. Four crystalline types of PVF$_2$ have been reported. The α-form (or Type II) is the one usually grown during crystallization from the melt[3–8]; it is electrically inactive due to the antiparallel arrangement of its molecular chains in the unit cell[5–8], although a polar form (α_p) has recently been produced in a high electric field[9]. The most common polar polymorph of PVF$_2$ is the β-form (or Type I) obtained by uniaxial drawing of α-PVF$_2$[7,8,10–12]; spherulites of this form have also been reported to grow from the melt[3,4] and from selected solvents[13]. Another polymorph (γ-form or Type III), whose unit cell is believed[8] to be only slightly different from that of β-PVF$_2$, has also been obtained under special conditions[3–5,14–16].

In order to produce these crystallographic variants of PVF$_2$ in an *oriented* form, samples have always been mechanically deformed by application of tensile or compressive forces at appropriate temperatures[5–8]. While the technique imparts high orientation to the samples, it also erases completely their existing morphology and sometimes introduces artefacts such as voids or defects. It would thus seem desirable to be able to examine PVF$_2$ samples which are not only well oriented, but which also preserve the morphological record introduced during crystallization.

The method used to this end is directional solidification – an extension of the zone melting process[17] – consisting basically of crystallization of the material within a sharp temperature gradient that traverses the length of the sample. While the important characteristics of this technique have been described in detail elsewhere[18–21], it is worth noting them briefly here. The sample consists of spherulites whose lamellar fibrils (beyond a short transition region) are all grown parallel to the direction of solidification. Orientation is thus not imposed by a *post facto* treatment as in the case of mechanical drawing or rolling, but is directly controlled by the crystallization process. As a result, while the samples are highly anisotropic, they still preserve the inherent morphological features (i.e. spherulitic and lamellar substructure) and crystallographic identity of their class.

Due to their special morphology, zone solidified films are expected to exhibit interesting variations of their mechanical properties in different directions. A number of authors have examined similar samples of other polymers[22–25]; however, these samples were of such geometry that it was possible to investigate mechanical behaviour in only one direction (i.e. either parallel or perpendicular to the direction of crystal growth). For example, Takayanagi[22] reported dynamic mechanical results along the longitudinal (*b*-axis) direction of a zone solidified polyethylene fibre, while Kwei *et al.*[25] examined the transverse mechanical behaviour of polyethylene and polypropylene thin films crystallized so as to possess two transcrystalline layers enclosing a random spherulitic layer of varying thickness. Consequently, the availability of unidirectionally oriented films of *large* lateral dimensions (i.e. > 3 cm) such as produced in this work, should enable us for the first time directly to compare the behaviour in *any* given directions; in this research, the directions selected were longitudinal (i.e. parallel to the oriented growth vector) and transverse (i.e. across the width of the specimen).

This paper presents a variety of results on zone solidified PVF$_2$. The crystallization processes and resulting morphology are described first. X-ray diffraction analysis, which allows us to elucidate the unit cell orientation in spherulites of PVF$_2$, is presented next. There follows a section on

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polarized infra-red spectroscopy of our samples, and the paper concludes with a dynamic mechanical study and some general remarks on piezoelectric behaviour of unidirectionally crystallized films of PVF$_2$.

EXPERIMENTAL

Materials

Directional solidification was performed on a number of commercial PVF$_2$ samples obtained from Kureha and Pennwalt Corporations (Kureha 1100, $\bar{M}_w$ = 207 000, $\bar{M}_n$ = 86 000; Kynar 821, $\bar{M}_w$ = 404 000, $\bar{M}_n$ = 215 000; Kynar 301, $\bar{M}_w$ = 39 000, $\bar{M}_n$ = 11 000 – all calibrated against polystyrene). The polymers were dissolved in dimethylformamide, filtered to remove heterogeneiteis that could act as potential nuclei, and cast on microscope slides for subsequent oriented crystallization. Films prepared by melt recrystallization in a heated press were also employed. Of these polymers, Kynar 821 exhibited the lowest rate of nucleation, thus yielding significantly better oriented films than the other polymers; as a result, all mechanical measurements were confined to this material.

Procedure

The supporting slides, containing polymeric films of lateral dimensions ~ 5 cm and thickness chosen from the range of 10 to 200 μm, were rigidly attached to the moving arm of a variable speed mechanical drive assembly (Harvard Apparatus Infusion Pump Model 975) and passed through the directional solidification stage described previously[26]. The films were usually crystallized open-faced so that their surface features would be available for subsequent examination by use of reflected oblique illumination or by electron microscopy. Films sandwiched between glass slides were also used occasionally, although ultimate separation of the unidirectionally solidified samples from their substrates was now much more difficult. In all cases, the entire apparatus was continuously kept under dry nitrogen. Zone velocities ranging from 0.6 μm/min (0.01 μm/sec) to 20 μm/min (0.33 μm/sec) were utilized at a temperature gradient of ~400°C/cm. After crystallization, the films could be separated from their substrates relatively easily by soaking in distilled water. The samples were then dried and examined in a number of ways.

Optical microscopy was performed by means of a Reichert–Zetopan universal microscope. Optical melting points, defined as the temperatures of disappearance of the last vestiges of birefringence, were obtained in a Mettler FP5 hot stage at a heating rate of 2°C/min. X-ray diffraction patterns were recorded by means of Ni-filtered CuKα radiation on a Laüe flat film camera placed 5.0 cm away from the sample. Infra-red spectra were recorded on a Perkin–Elmer Model 621 spectrophotometer equipped with a gold wire grid polarizer. The sample was positioned at 45° with respect to the slit, and the polarizer at 45° and 135° in order to minimize the effects of machine polarization.

Dynamic mechanical properties were measured at a frequency of 110 Hz using a Rheovibron dynamic viscoelastometer, Model DDV-II[22]. Data were taken between −180° and 160°C by subjecting the sample to a sinusoidal strain (amplitude 0.42%) superposed on a constant (static) strain which ranged from about 0.2% at −180°C to less than 2% at 100°C, increasing to about 5% at 160°C. These static strains imposed during the dynamic measurements are not expected to induce significant non-linear effects[27,28] except perhaps at temperatures much above 100°C. The films were heated at a rate of 1.5°C/min by means of a specially designed oven, and the temperature was monitored using two thermocouples placed near the ends of the strip (i.e. ~2 cm apart); sample temperature was defined as the average of these two readings, whose difference was generally less than 1.5°C. Film thicknesses (typically about 50 μm) required for calculation of the modulus were determined from the density and from measurements of the other two dimensions of the strip.

RESULTS AND DISCUSSION

Zone solidification was able to provide varying degrees of orientation at growth rates below approximately 10 μm/min (0.17 μm/sec). At such rates, the average degree of geometrical isotropy* for all samples never fell below 0.6, indicating only marginal orientation due to profuse primary nucleation. While the KF-1100 and Kynar 821 films exhibited higher orientation at lower zone velocities, the remaining samples did not; apparently, the critical number of heterogeneous and pseudo-homogeneous nuclei in the latter samples that survive in the melt is too high to allow effective orientation by this process. At growth rates of 3–4 μm/min (0.05–0.07 μm/sec), the effectiveness of orientation reached a maximum from which it did not deviate significantly even at rates as low as 0.6 μm/min (0.01 μm/sec). The KF-1100 samples gave typical degrees of geometrical isotropy down to about 0.3, whereas Kynar 821 provided by far the best orientation, yielding values for ϵ as low as 0.07, with some spherulites exceeding 1 cm in length. One should keep in mind, however, that in most films occasional minute discontinuities arising from fluctuations in sample motion or in the temperatures of the heater and cooler were practically unavoidable.

Morphology

The typical appearance of zone solidified thin films of PVF$_2$ is seen in *Figure 1a*. This low magnification, while obscuring fine detail, serves best to illustrate the overall pattern produced by this process: long spherulites growing in the direction of solidification and extending throughout the sample, with subsequent primary nucleation being relatively infrequent. It is noteworthy that new spherulites generally tended to nucleate very close to the front of the oriented matrix, more so than in any of the other polymers directionally solidified so far[18–21,26,29]. Visual observation during the crystallization process showed many spherulites nucleating almost exactly at the crystallizing interface of oriented fibrils with the melt. This attests to the efficacy of our nucleation control measures: most crystalline remnants that could potentially promote pseudohomogeneous or self-nucleation ahead of the oriented matrix have been destroyed or neutralized in the melt. This has been achieved by increasing the *duration* of superheating while keeping its *mangitude* relatively low so as to minimize degradation[18,20]. At representative zone velocities of, say, 1–3 μm/min (0.016–0.05 μm/sec) the current in the heater was adjusted to produce a mol-

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* The degree of geometrical isotropy, ϵ, is defined for a directionally solidified spherulite as the ratio of the lengths of two mutually perpendicular axes passing through the nucleus; the one in the numerator is parallel to the family of isotherms, whereas the one in the denominator is parallel to the direction of solidification[19]. Thus, ϵ ranges from 0 (for a perfectly oriented spherulite) to 1 (for a totally random one).

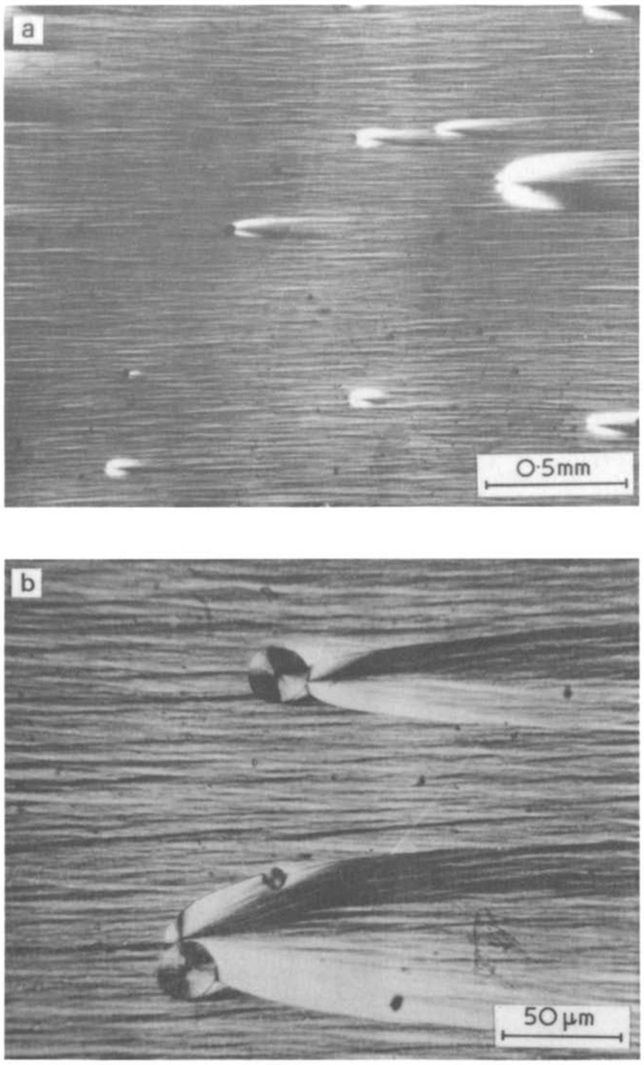

Figure 1 **(a) General appearance of PVF_2 directionally solidified from left to right. (b) Higher magnification of a region of initiation of two oriented spherulites**

ten zone of about 3 mm width, this caused the maximum temperature in the melt to remain below 200°C while allowing the melt residence time to be as long as 16–50 h. The resulting initiation of new spherulites so close to the oriented front is of particular importance for overall orientation because it minimizes both the length and the width of the curved transition region required to render these spherulites parts of the oriented matrix[12]. Consequently, the percentage and length of lamellar fibrils within the sample that are not parallel to the direction of solidification are correspondingly minimized as well.

Although PVF_2 can crystallize from the melt in a number of spherulitic forms[3,4], the appearance of *Figure 1a* is totally homogeneous: not only are there no complete spherulites of multiple types seen in this *Figure*, but even the familiar transformations during crystallization to faster growing species – as encountered in isotactic polypropylene[20] and even–even polyamides[21,29] – are also apparently absent. However, close inspection at high magnifications, as for example in *Figure 1b*, reveals that a few, more or less circular spherulites of low birefringence are interspersed among the highly elongated ones. The two spherulitic species seen in *Figure 1b* were identified by their melting points. In all cases, the actual melting points agree well with the results of Prest and Luca[3] (as well as with our own measurements on isothermally crystallized samples), and show that the oriented phase consists of α-type spherulites. The small, unoriented spherulites melt at a temperature attributed to the β-polymorph[3]; for the sake of consistency with the existing literature, we shall refer to them as β-spherulites, although their crystallographic identity is in question[30]. Specifically, for the case of films used in dynamic mechanical studies, the melting points were found to be $T_{m\alpha} = 171-172°C$ and $T_{m\beta} = 178°C$. These values indicate a crystallization temperature of ~153°C, which is in agreement with the T_c expected from the applied zone velocity of 3 µm/min[30]; furthermore, they show that despite the long residence times in the melt, degradation must have been controlled to acceptable limits.

Let us return, however, to the examination of the two types of spherulite observed in the oriented crystallization of PVF_2 by noting some important features which are revealed at yet higher magnifications, as seen, for example, in *Figure 2*. Contrary to initial appearances, these spherulitic forms are not always independent of one another; rather, the β-type was found frequently to initiate growth of the α-form. This is distinctly seen in *Figure 2*, where transformations in growth of a β-type spherulite at three different points along its perimeter have initiated crystallization with the α-unit cell. Clearly, the much faster growth of α-type spherulites (up to an order of magnitude higher than that of their β-counterparts) causes very rapid encirclement of the β-precursors, whose further growth in all directions is thus destined to terminate very soon after occurrence of the initial discontinuity. The high magnification of *Figure 2* also reveals the well-known concentric banding of α-type spherulites, which is so dense that it escapes resolution at magnifications employed to study the overall features of directionally solidified samples (e.g. *Figures 1a* and *1b*). The bandwidth in all cases is of the order of only 0.8 µm, thus representing one of the tightest twists of molecular orientation among all polymers. In contrast, the small β-spherulites exhibit much coarser and more poorly coordinated features when viewed between crossed polarizers.

To summarize our morphological results, zone solidification of PVF_2 produced predominantly very well oriented (i.e. highly elongated) banded spherulites of the non-polar α-form. Spherulites of β-PVF_2 were only very rarely oriented, and then only slightly so; this is mostly due to frequent incidents of α-growth initiation at the perimeters of β-

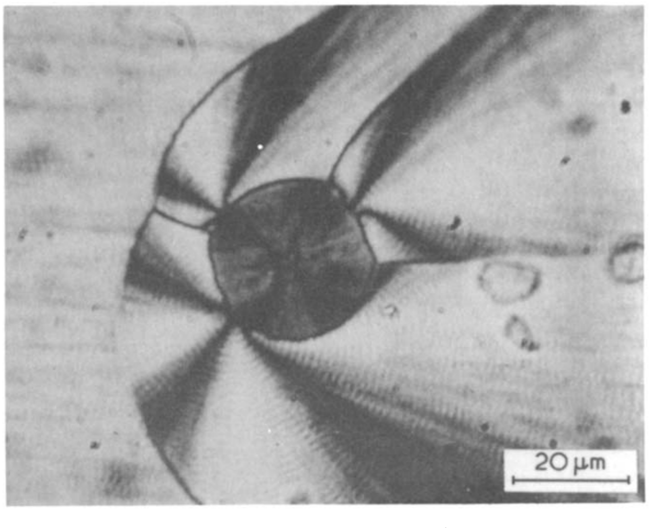

Figure 2 β-type spherulite causing initiation of α-type spherulites at three points on its perimeter

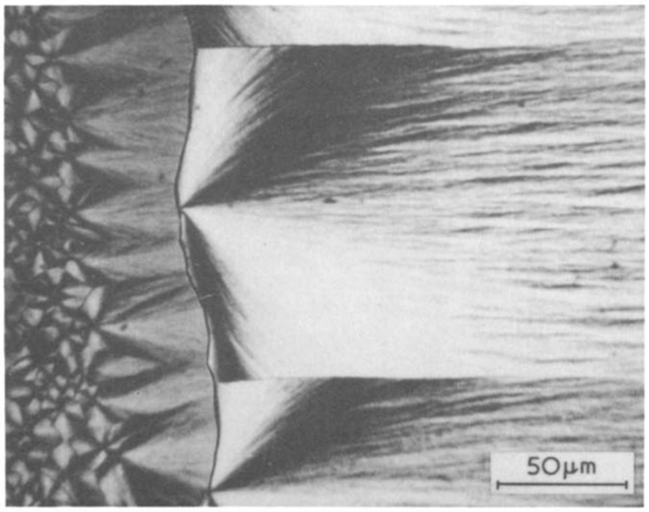

Figure 3 Initial region in PVF$_2$ directionally solidified at 0.6 μm/min

spherulites, which resulted in their rapid envelopment by the α-form. Although γ-PVF$_2$ has been reported to grow isothermally from the melt above ~157°C[3,4], it was absent among our directionally solidified specimens, even though they were crystallized at zone velocities as low as 0.6 μm/min (0.01 μm/sec) corresponding to $T_{c\alpha}$ = ~159°C. One might possibly attribute the absence of γ-spherulites in our experiments to the effects of prolonged residence in the superheated melt. This would be consistent with infra-red data of Prest and Luca[3], which showed significant reduction of absorption peaks attributed to the γ-phase after lengthy heat treatments. The preferential primary nucleation of the α-phase, its much faster growth rate, as well as the spontaneity of its initiation from β-type spherulites, all show that this form is kinetically favoured over the other two. In addition Hasegawa *et al.*[8,31] have also shown by use of potential energy calculations that steric hindrance and electrostatic interactions cause the β- and γ-polymorphs to be less stable than the α-type.

In general, we may venture to predict that it is highly improbable that large films containing predominantly β- or γ-type spherulites will ever be obtained by directional solidification. The reasons for this are apparent in *Figure 3,* which shows the initial region in a PVF$_2$ sample unidirectionally crystallized at an extremely slow rate (0.6 μm/min). Under these conditions, the first spherulites to form belonged to the β-type and began to orient quite promisingly. However, it is seen in the centre of this Figure that if the α-phase is initiated at even a *single* point along the oriented front, it will immediately spread across the entire front and occupy the rest of the sample. In directionally solified polypropylene[20] or polyamides[21,29], similarly initiated phases permit formation of considerable expanses of the slower growing polymorphs since they crystallize only about 5–80% faster. When, however, such crystallization proceeds at a rate faster by up to almost 800% (as is the case here), chances for any significant growth of the slower polymorph are virtually eliminated.

X-ray diffraction analysis

Wide-angle X-ray diffraction patterns of PVF$_2$ polymorphs have been presented and discussed by a number of authors[7–10,12,16]. As has been mentioned before, α-type spherulites usually transform to β-type oriented fibrils during mechanical drawing; nevertheless, cases have been reported where the α-unit cell is preserved in large part[8]. As a result both powder patterns and fibre diagrams of the α-modification have been obtained; neither of these, however, allows determination of unit cell orientation along the spherulitic radius.

This orientation can be established in our directionally solidified samples by use of *Figure 4a*; this depicts the flat film transmission pattern produced by PVF$_2$ specimens zone solidified from top to bottom, with the X-ray beam normal to the planes of the samples. The major reflections are identified in *Figure 4b* based on the indexing summarized in *Table 1,* which shows excellent agreement between observed interplanar spacings and those calculated for the α-unit cell. From the meridional disposition of (020) reflections we conclude that the *b*-axis of the unit cell is parallel to the direction of solidification. This is confirmed in *Table 1,* where the observed interplanar angles (φ) of all major reflecting planes with

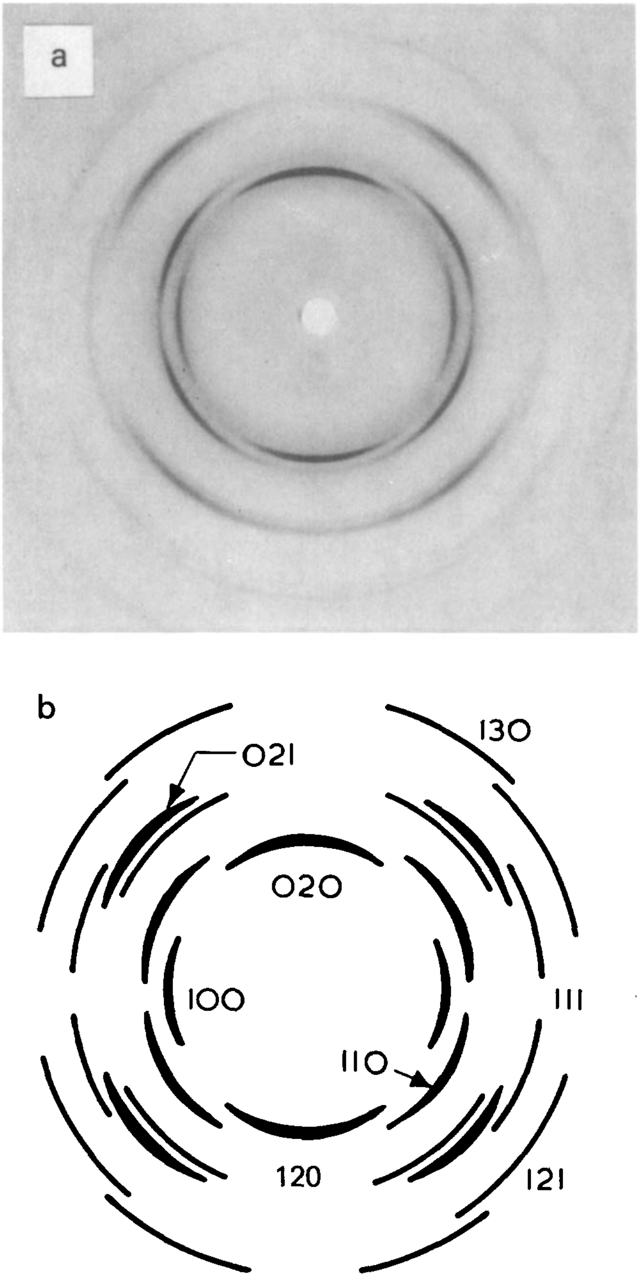

Figure 4 (a) Wide angle X-ray diffraction pattern of unidirectionally crystallized PVF$_2$; direction of solidification vertical; (b) indices of the major reflections

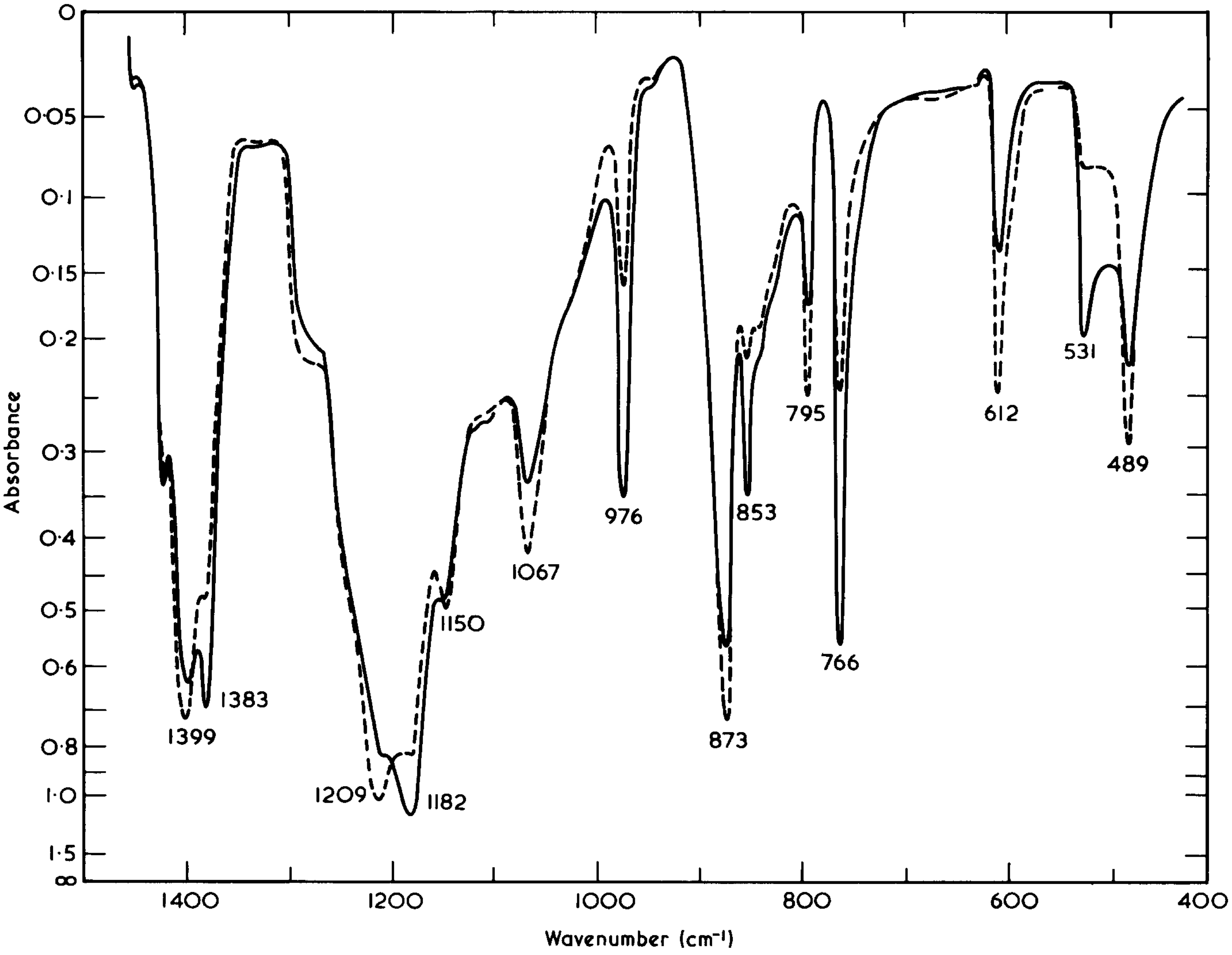

Figure 5 Polarized infra-red spectra of zone solidified PVF$_2$. Full curve, electric vector parallel to the direction of solidification; broken curve, electric vector perpendicular to the direction of solidificationY

Table 1 Indexing of diffraction pattern from directionally solidified α-type spherulities of PVF$_2$

Reflection	d_{obs} (Å)	d_{calc} (Å)	ϕ_{obs}	ϕ_{calc}
100	4.98	4.96	90°	90°
020	4.80	4.82	0°	0°
110	4.39	4.41	62.5°	62.8°
120	3.48	3.46	44°	44.2°
021	3.31	3.34	46°	46.2°
111	3.19	3.19	72.5 °	70.7°
121	2.78	2.77	53.5°	55.0°
130	2.69	2.70	33°	32.9°

the (020) family are in close agreement with their calculated values.

Thus, it is seen that in some respects orientation in directionally solidified α-type PVF$_2$ films is not unlike that in drawn β-type samples. In both cases, the dipoles are arranged normally to the orientation direction, i.e. along the *a*-axis in samples zone solidified with *b* radial, and along the *b*-axis in drawn films where *c* is the fibre axis. Similarly, cylindrical symmetry prevails in both cases about the unique direction in the samples. The main differences include the electrical nature of the two unit cells (the β-cell is polar while the α-cell is electrically neutral) as well as the crystalline substrate of the two types of sample (fibrillar *versus* lamellar, respectively).

Infra-red analysis.

Polarized infra-red spectra with the direction of vibration of the electric vector parallel and perpendicular to the direction of solidification are shown in *Figure 5*. The spectra are fully representative of the α-polymorph[5,6,32] and clearly reflect the high degree of orientation present in the sample. The major absorption peaks are given in *Table 2* which also contains calculated dichroic ratios, D, and angles, θ, between the transition moment of each infra-red-active dipole and the direction of solidification. Parallel and perpendicular absorbances were calculated after subtracting the 'baseline absorbance', obtained by drawing tangents to the curve immediately to the right and left of the bands in question[33,34]. The angle θ is computed from the relation $D = 2\cot^2\theta$, which is appropriate for uniaxially drawn polymers[35,36]. This equation takes into account the fact that the molecular chains are parallel to the draw direction, while the crystallites possess otherwise full cylindrical symmetry about the *c*-axis. Hence, this definition of θ may be adapted to our case on the basis of the X-ray results which show the

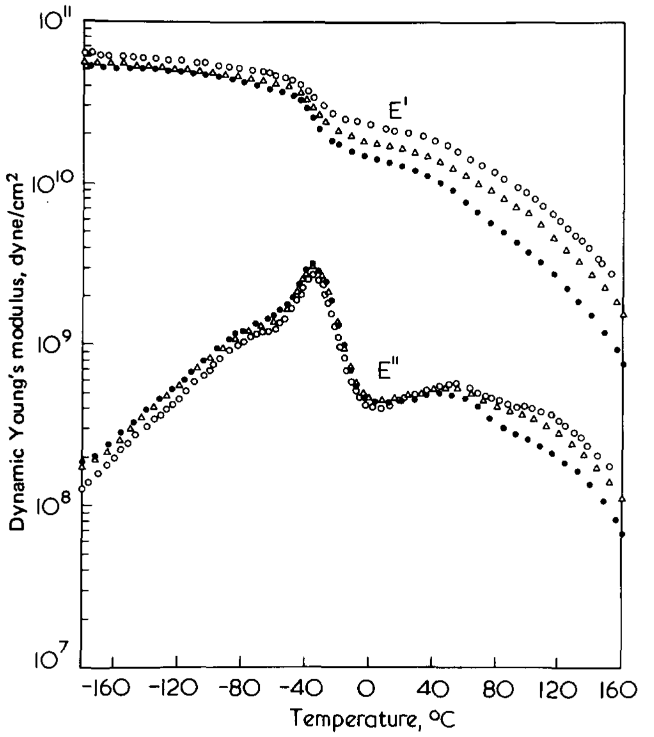

Figure 6 Temperature variation of the in-phase (E') and out-of-phase (E'') components of Young's modulus for PVF$_2$ samples. ○, Directionally solidified sample ($\parallel$); ●, directionally solidified sample ($\perp$); △, isothermally crystallized sample

b-axis to be the unique direction in zone solidified α-PVF$_2$. Clearly, then, for all absorption bands for which $\theta > 54.73°$ the parallel absorption will be less than the perpendicular, which indicates that the transition moment of the dipole in question is preferentially aligned normal to the direction of solidification; dipole moments more closely oriented parallel to the b-axis will, of course, have $\theta < 54.73°$. It should be noted that this treatment neglects the effects of misorientation and of infra-red activity from amorphous regions[34]; moreover, the experimental determination of absorbances at frequencies between 1400 and 1150 cm^{-1} is less accurate than in the rest of the spectrum, because of broader peaks and shoulders which make determination of the baseline absorbance ambiguous.

The infra-red results presented in *Figure 5* and *Table 2* are thus in agreement with our expectations from the morphological and X-ray diffraction study of directionally solidified PVF$_2$. Thus, the absorption bands are all characteristic of an oriented film crystallized with the α-unit cell. Furthermore, all absorption bands which appear in parallel polarization in drawn α-PVF$_2$ (i.e. those at 1399, 1290, 1150, 612 and 489 cm^{-1}) are now perpendicularly polarized in our specimens, as one would expect since the molecular chains are disposed normally to the macroscopic direction of oriented growth. Among bands which in mechanically drawn samples are perpendicularly polarized, those whose effective transition moments lie closer to the b-axis should now appear in parallel polarization. Such a case is seen, for example, in the strongly polarized band at 531 cm^{-1}, originating from the normal bending mode of the $-$CF$_2$ dipole, whose net transition vector in the unit cell is preferentially inclined toward b.

Dynamic mechanical behaviour

The dynamic Young's modulus was measured as a function of temperature under a constant frequency. To minimize the degree of uncertainty that could arise from a single temperature sweep, the measurements were repeated three times on three different samples over the same temperature range. Measurements were carried out on zone solidified α-PVF$_2$ films in the directions parallel ($\parallel$) and perpendicular ($\perp$) to the direction of solidification, as well as on samples isothermally crystallized at 152°C for 5 h (which approximates the conditions prevailing during zone solidification). Both types of sample had the same density of 1.785 g/cm^3, which corresponded to a crystallinity of about 47%, assuming a density of 1.92 g/cm^3 for the α-crystal[8] and 1.68 g/cm^3 for the amorphous fraction[37].

Comparison of the results showed several interesting features and trends which could best be described by referring to the typical curves shown in *Figure 6*. As with the isothermally crystallized sample, the plots for out-of-phase moduli (E'') of the oriented sample exhibit four relaxation regions centred near 100°C (α_1), 50°C (α_2), -38°C (β), and -70°C (γ), which have been attributed to molecular motions associated with crystalline regions (100°C and 50°C) and with amorphous regions (-38°C and -70°C)[38–41]. However, there are differences in the magnitudes of E'' for the two directions over the entire temperature range, these being particularly significant above 40°C and below -80°C. At temperatures below 20°C, $E''(\perp) > E''(\parallel)$, while at temperatures above 20°C the trend is reversed. In addition, the $E''(\parallel)$ plot is marked by a distinct α_1 peak which is barely visible in the $E''(\perp)$ plot. The stronger α_1 dispersion in the $E''(\parallel)$ curve and its close proximity to the α_2 dispersion have apparently caused a shift in the α_2 peak to a higher temperature [50°C for $E''(\parallel)$ *versus* 44°C for $E''(\perp)$]. The directional dependence of dynamic response is also evident in the plot for the in-phase modulus, E', where $E'(\perp)$ is seen to be consistently smaller than $E'(\parallel)$ and to drop sharply at elevated temperatures.

Another point of interest concerns the E' and E'' curves for the isothermally crystallized sample: these fall between the corresponding curves for the oriented samples in the two directions, but in such a way that they tend toward the transverse curve on the low temperature side (<20°C) and the parallel curve on the high temperature side.

The differences in observed behaviour are believed to be associated with the orientation of lamellar crystals since all samples had the same density and, presumably, the same degree of crystallinity. Although quantitative correlation may be subject to experimental limitations, it is interesting to note that the general trends are qualitatively consistent

Table 2 Infra-red analysis of directionally solidified PVF$_2$

Observed frequency (cm^{-1})	Dichroic ratio ($D = A_{\parallel}/A_{\perp}$)	θ
1399	0.62	61.0°
1383	3.02	39.1°
1209	0.38	66.5°
1182	2.08	44.4°
1150	0.67	60.0°
1067	0.57	61.9°
976	2.54	41.6°
873	0.69	59.6°
853	3.21	38.3°
795	0.54	62.6°
766	2.56	41.5°
612	0.50	63.3°
531	4.55	33.5°
489	0.60	61.3°

with a mechanically equivalent model suggested by Takayanagi[22]. Thus, in the case of directionally solidified α-PVF$_2$ which could be assumed to be morphologically similar to the b-axis oriented polyethylene treated by Takayanagi[22], the crystalline and amorphous phases are more or less joined 'in parallel' in the direction of oriented growth, and 'in series' in the transverse direction. Accordingly, the relaxation behaviour of the oriented sample should be dominated by contributions from the crystalline phase along the parallel direction (parallel model) and from the amorphous region in the transverse direction (series model), in agreement with the results of *Figure 6*. Similarly, the rapid decline in E' (⊥) at high temperatures could be explained by the significant softening of the amorphous fraction in the series model. For the isothermally crystallized sample having a random orientation of lamellar fibrils, the two phases are likely to be coupled both in parallel and in series in nearly equal proportions. Consequently, the sample should display a behaviour intermediate between those of the parallel model (∥ direction) and the series model (⊥ direction), as observed in *Figure 6*.

In addition to the dynamic mechanical measurements, the Rheovibron viscoelastometer was also used to test the piezoelectric response of directionally solidified α-PVF$_2$. Films were metallized with Al for poling at 200 kV/cm and 90°C for 12 h. The samples were then cooled with the field on before being annealed at 60°C for 16 h while short circuited. Repeated attempts to pole the samples at higher fields were unsuccessful due to breakdowns in the directionally solidified samples. This may be associated with the extremely slow growth rates and the prolonged residence of the polymer in the molten state, which could lead to significant localized segregation of lower molecular weight chains and 'impurities'. Consequently, our piezoelectric results are intended only to compare the behaviour of PVF$_2$ films of varying morphology at low poling fields, and may not necessarily predict the response at high fields – if poling of large samples of zone solidified PVF$_2$ is indeed possible at such high fields.

Piezoelectric measurements performed at a mechanical excitation of 110 Hz and at room temperature yielded a value for d_{31}, the piezoelectric constant[*], equal to 0.0423 pC/N for our directionally solidified specimens. This is the same (0.0420 pC/N) as was obtained from an isothermally crystallized sample displaying a random spherulitic morphology. It is also approximately two orders of magnitude lower than the value for a predominantly β-type film uniaxially drawn at 70°C (extension ratio 4) and then poled and annealed under identical conditions, for which d_{31} was found equal to 2.19 pC/N. It is thus seen that zone solidification of PVF$_2$ did not provide any advantage in piezoelectric response over isothermal crystallization from the melt at low or intermediate temperatures[3]. This is primarily due to crystallization in both cases with the α-unit cell; the high orientation imparted by zone solidification was shown not to promote preferential alignment of dipoles normal to the film surface any more than does the isothermal process, resulting in identical piezoelectric behaviour in both types of sample. The much higher piezoelectricity of drawn films at this low field may result from the relative polarizabilities of the two crystalline forms as functions of poling strength; while 200 kV/cm is adequate to induce polarization in the β-phase, α-type crystals require much higher fields to transform to a polar form[9].

CONCLUSIONS

The properties of directionally solidified PVF$_2$ have been seen to reflect strongly the type of orientation introduced by this technique. Long α-type spherulites with their b-axes along the oriented growth vector were obtained almost exclusively; a few β-type spherulites were observed, but these were restricted to very small sizes due to their tendency to transform during crystallization to the much faster growing α-form. The dynamic mechanical behaviour of zone solidified films in the longitudinal and transverse directions, as well as its relationship to that of randomly crystallized samples is in qualitative agreement with Takayanagi's two-phase model[22]. Piezoelectric response at low poling fields is small and commensurate to that of a random spherulitic film, due to the non-polar nature of α-unit cells and the non-unique disposition of dipole vectors in both cases.

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[*] Here, the first subscript refers to the film normal and the second to the direction of solidification

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