Crystalline transformations in spherulites of poly(vinylidene fluoride)

Andrew J. Lovinger
Bell Laboratories, Murray Hill, New Jersey 07974, USA

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Parts of poly(vinylidene fluoride) spherulites of the α-phase undergo a transformation to the higher-melting γ-form when crystallized at high temperatures. As a rule, this transformation originates at the periphery of α-spherulites where their lamellae are in contact with, and oppositely directed to, lamellae of γ-spherulites; the latter are formed only at high temperatures. The transformation on then retreats towards the nuclei of α-spherulites at a slow ($\sim 10^{-4}$ μm s^{-1}), linear rate, which increases with temperature. At very high temperatures, this transformation is also initiated at some α-nuclei; a few of the α-spherulites also exhibit areas of the high-melting phase irregularly dispersed within their interiors. In samples crystallized below ~154°C, the transformation is of very limited extent, even after prolonged annealing at higher temperatures.

INTRODUCTION

Poly(vinylidene fluoride) (PVF$_2$ or PVDF) exists in four crystalline modifications. The most common of these is the α-form, whose unit cell contains two molecular chains of $TGT\bar{G}$ conformation[1]. The β-form, commonly obtained by mechanical deformation of α-PVF$_2$, consists of molecules in essentially an all-*trans* (TT) conformation which are packed orthorhombically in a polar unit cell[1]. Recent X-ray evidence[2] showed that the unit cell of γ-PVF$_2$ is also probably orthorhombic and polar; a crystal structure analysis[3] yielded a $T_3GT_3\bar{G}$ chain sequence as most likely for this polymorph. The fourth form (α_p) is a polar version of α-PVF$_2$, obtained as a result of the orienting action of high electric fields[4]. These crystalline modifications of PVF$_2$ are also known as forms II, I, III, and IV respectively.

Although the main interest in PVF$_2$ arises from its piezoelectric activity[5], there is increasing evidence that this polymer is morphologically extraordinary, as well. Gianotti *et al.*[6] were the first to observe two types of spherulite upon crystallization of PVF$_2$ from the melt; large spherulites of the α-form are the most common, while smaller spherulites, attributed to the γ-polymorph, are seen less frequently and only at high temperatures. The very thorough study of Prest and Luca[7] found the same two spherulitic species, but there the evidence pointed to the β-form as the constituent of the smaller spherulites. This issue is still confused, because recent X-ray-[8] and electron-[9] diffraction patterns from such spherulites are predominantly consistent with the γ-form[2]; this and other reasons (i.e. occasionally disturbed morphological features and suggestions of inclusions from a second phase) have led us to use the term 'mixed spherulites' for this crystalline species.

In addition to this wide morphological diversity, two types of crystalline transformation have also been reported in melt-crystallizing poly(vinylidene fluoride). The first of these involves a change in spherulitic form at the growth tips of crystallizing lamellae and is kinetically favoured[8]. In the case of PVF$_2$, the faster-growing α-form is frequently initiated at the lamellar fronts of mixed spherulites[8,10]; this phenomenon has also been observed in isotactic polypropylene[11] and even–even polyamides[12]. A much more interesting kind of transformation has been reported by Gianotti *et al.*[6] and Prest and Luca[7] during high-temperature annealing of PVF$_2$; it is described as a solid-state transformation of α-spherulites to a higher-melting form, and is of a kind that (to date) appears unique to PVF$_2$ among all polymers. On the basis of infra-red data, Gianotti *et al.*[6] ascribed the transformed spherulites to the β-form, while Prest and Luca[7,13], employing a much more detailed infra-red investigation, attributed them to the γ-form. The latter authors also suggested that this $\alpha \rightarrow \gamma$ transformation is initiated at the nuclei of existing α-spherulites, from which it then proceeds radially outwards.

To obtain a better understanding of the morphogenesis and characteristics of this transformation, PVF$_2$ samples were crystallized under different conditions and investigated by optical and electron microscopy. Results of this morphological study are reported in this paper. Further research has also shown that this transformation is accompanied by a highly unusual inhomogeneous thermal degradation; this degradation is described in a separate paper[14].

EXPERIMENTAL

The samples studied were compression-moulded thin films of Kynar 821, a Pennwalt Corp. resin. Its molecular weight, determined by gel-permeation chromatography of 0.5% PVF$_2$ solutions in *N*,*N*-dimethyl formamide by use of a Waters Liquid Chromatograph Model 244, and calibrated against polystyrene, was $\bar{M}_w = 541\,000$ and $\bar{M}_n = 337\,000$. It has been found[8,14] that this polymer is fairly typical of the Kynar family of resins, and that PVF$_2$ resins manufactured by Kureha Corp. generally show the same behaviour as their Pennwalt counterparts, but at slightly

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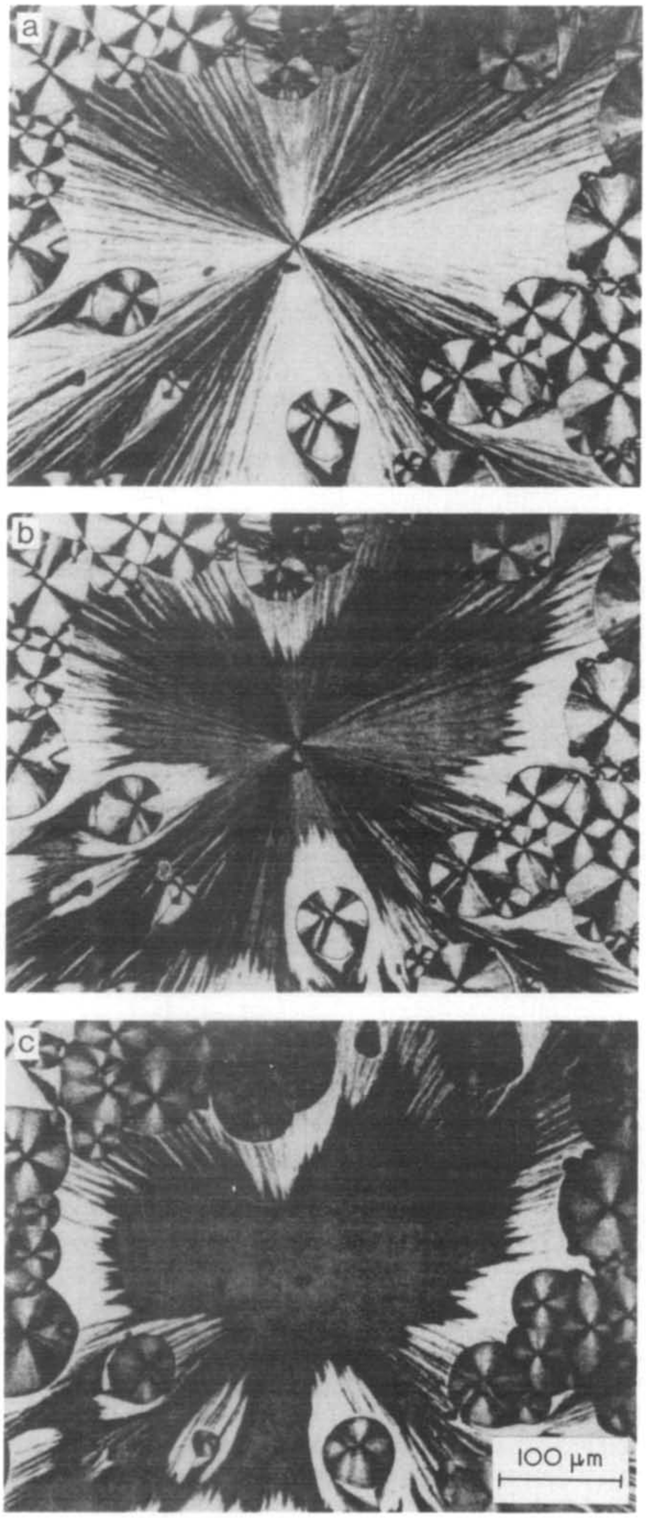

Figure 1 Melting behaviour of an α-spherulite crystallized in the vicinity of mixed spherulites. Sample at 158°C for 3 days. (a) 158°; (b) 172°; (c) 180°C

higher temperatures[7,8]. Isothermal crystallizations took place on glass-supported films within a Mettler FP52 microscope thermal stage under flow of dried N_2, or in a vacuum oven. Samples for electron microscopy and diffraction were deposited from dilute solution in DMF on freshly cleaved mica. After evaporation of the solvent, the polymer films were held at ~220°C for up to 1/2 h, prior to crystallization at the desired temperature. At predetermined times, the temperature was gradually raised to above the melting point of the α-phase (but below those of the mixed spherulites or of the transformed species), whereupon the samples were rapidly quenched to the boiling point of nitrogen. This treatment allowed the transformed regions to be clearly delineated within the outlines of the original α-spherulites. The thin films were then shadowed, carbon coated, floated off their substrates, and placed on copper grids in the usual manner prior to examination in a Philips EM200 transmission electron microscope.

RESULTS AND DISCUSSION

Annealing of melt-crystallized PVF_2 at high temperatures results in formation of a new, highest-melting phase; its melting points are those found by Prest and Luca[7], i.e. they lie between 187°C and 194°C. Also in agreement with these authors[7], infra-red evidence[14] suggests that these highest-melting crystals belong to the γ-form. These γ-crystals are the result of a transformation which occurs in some parts of some α-spherulites after crystallization in the temperature range in which mixed γ-spherulites are also grown.

The general features of this transformation at moderately high temperatures (i.e. ~155°C–162°C) are seen in the polarized micrographs of *Figure* 1: *Figure* 1*a* depicts a large α-type spherulite surrounded by numerous small γ-type spherulites, all of which had been crystallized isothermally at 158°C for 3 days. As the temperature is raised to 172°C (the melting point of α-spherulites crystallized at 158°C), it is seen that the birefringence of only parts of the α-spherulite begins to decrease — specifically those parts that are not in contact with the small spherulites (see *Figure* 1*b*). In agreement with the results of Gianotti *et al.*[6] and Prest and Luca[7,13], these birefringent portions of the original α-spherulite are the highest-melting species, surviving fusion of both α- and mixed spherulites (*Figure* 1*c*). From many micrographs of this kind, it was seen that, except for crystallization at very high temperatures (162°C or above) where other processes (discussed below) also take place, these highest-melting species appear only at the junctions of α- and mixed spherulites; they are generally absent at the boundaries between α-spherulites and at α-nuclei.

The morphogenesis of the transformation leading to this highest-melting phase may be studied with the aid of *Figure* 2, where the melting behaviour of α-spherulites is seen as a function of contact time with their small, mixed counterparts. In the case of *Figure* 2*a*, where the total thermal treatment (i.e., crystallization and annealing) lasted 20 h at 159°C, the transformation is clearly seen to be restricted to the tips of α-lamellae that are in contact with mixed spherulites. Furthermore, this occurs overwhelmingly at those α-tips that are oppositely directed to lamellar tips of the small spherulites; α-fibrils at large angles to the radii of adjoining mixed spherulites (i.e., nearly tangential to the periphery of the latter) do not appear to transform at this stage. The more extended heat treatment of *Figure* 2*b* is seen to cause a pronounced increase in the radial length of transformed α-lamellae. In addition, fibrils encircling the small spherulites have now joined the high-melting species. The same is true for the central region of the original α-spherulite, although this is so only because the transformation was allowed to reach the nucleus (rather than through initiation at the spherulitic centre).

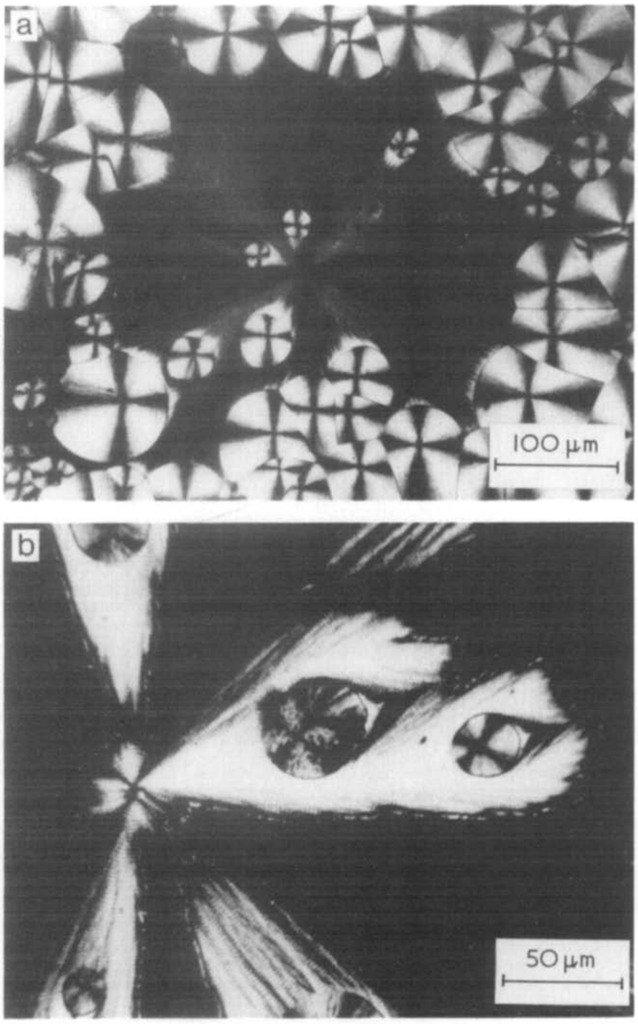

Figure 2 Appearance of α-spherulites grown at 159°C in contact with mixed spherulites as a function of time: (a) t = 20 h; T_{photo} = 171°C; (b) t = 100 h; T_{photo} = 177°C

From the above observations, we may propose a mechanism for this crystalline transformation in poly(vinylidene fluoride), as follows (see *Figure* 3): The transformation occurs only at temperatures where both α- and mixed spherulites are grown from the melt (i.e. generally above 153°C); as a rule, it does not begin before the two spherulitic types have come in contact with each other (exceptions to this rule at higher temperatures are discussed below). The transformation is apparently initiated in molecules of α-spherulites that are in contact with crystalline stems of mixed spherulites (M in *Figure* 3); chain conformation in the latter is known[3] to comprise TTT sequences, which are common to both β- and γ-unit cells. The transformation is therefore seen first in Region 1, where the radii of the two types of spherulite are directed oppositely, causing their respective lamellae to be extensively intermeshed. Where fibrils of the two spherulites are at large angles (e.g. in region 5, *Figure* 3), the transformation proceeds at a much slower rate, causing its effects to become visible only after prolonged heat treatment; this is probably due to the generally unfavourable register of crystalline segments of the two polymorphs, attributable in great part to the 'insulating' effects of the amorphous layers. As Prest and Luca have shown by infra-red spectroscopy at high temperatures[7] (see also ref. 14), the highest-melting species belong crystallographically to the γ-phase. Therefore, it appears that the transformation proceeds from stem to stem by changing the original $TGT\bar{G}$ conformation to that of the γ-form (i.e., $T_3GT_3\bar{G}$). However, there is no simple pattern of successive bond rotations along α-chains that would convert them to γ; the simplest involves change of every G bond to T and of every second G bond to G. This may take place by a kind of crankshaft-like motion about G-bonds, altering the original $GT\bar{G}TG$ segments to TTGTT (or about $\bar{G}$-bonds, changing $\bar{G}TGT\bar{G}$ segments to $TT\bar{G}TT$). Such a process would be thermodynamically favoured, since the α- and γ-phases are, respectively, the lowest- and highest-melting of all PVF_2 polymorphs[7]. An activation-energy barrier is implied by the fact that, in this temperature range, presence of TTT sequences (available initially in mixed spherulites) is required to start this process and to transmit it from stem to stem.

In this way, the transformation initiated in region 1 (*Figure* 3) proceeds along the lamellae of the α-spherulite (direction 2), advancing towards the nucleus, N, i.e. in a direction opposite to that of ordinary spherulitic growth. At the same time, this process takes place across lamellae, as well (direction 3), but at a much lower rate because it must now penetrate the amorphous barrier of their broad faces which cannot effectively transmit the required conformational changes. Of course, once part of a lamella has transformed in this manner (i.e. across its faces), further transformation along the lamella (direction 4) proceeds both backwards and forwards at the original higher rate. As a consequence of this combination of processes (fast transformation along lamellae and slow transformation across them), the entire α-spherulite, including both the nucleus and the curved fibrils around mixed spherulites (region 5), may eventually change to the high-melting form. Because of its focal position, the nucleus, once transformed, causes the transformation to advance radially outwards in all directions in a manner analogous to ordinary crystal growth.

The above model is also consistent with electron microscopic evidence which shows that the transformation is not accompanied by any observable morphological change. This is seen in *Figure* 4, obtained at relatively low magnification in the electron microscope

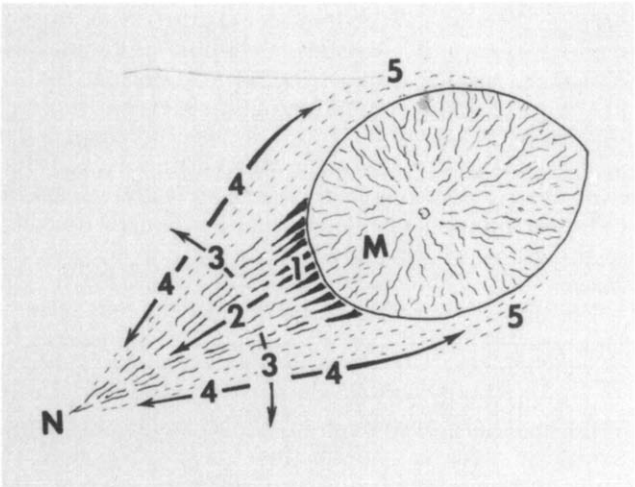

Figure 3 Schematic diagram of the evolution of the solid state transformation (see text)

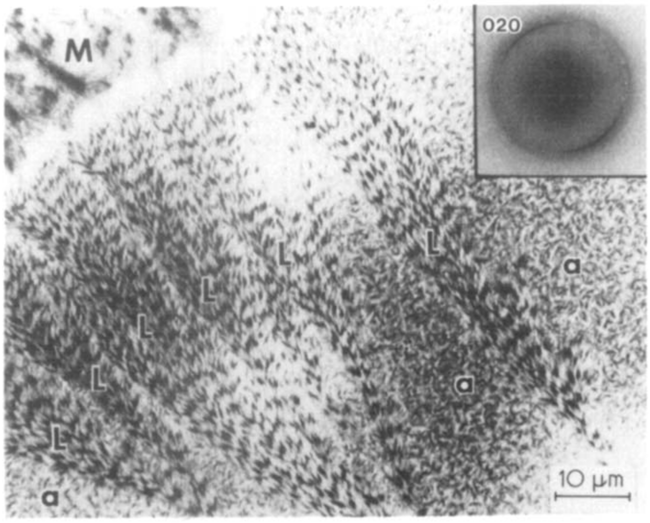

Figure 4 Electron microscopic appearance of transformed lamellae, and their electron diffraction pattern. The sample was crystallized at 160°C for 95 h, heated to 178°C, and quenched to liquid nitrogen temperatures

and depicting a sample crystallized at 160°C for 95 h prior to heating to 178°C and subsequent quenching to liquid nitrogen temperatures. This treatment succeeds in melting out the untransformed regions of the original α-spherulite, which reappear as the mottled background (a) in *Figure* 4 due to their rapid recrystallization during quenching. The edges of the mixed spherulite which originated the transformation are at the top left corner of this micrograph (M). In this Figure, the high-melting species appear to be twisted lamellae (L), indistinguishable from their original α-counterparts. This morphological identity persists all the way down to the finest features resolvable in the microscope at very high magnifications. The accompanying electron-diffraction pattern of the 178°C melting survivors (shown in correct orientation in *Figure* 4) is in agreement with the γ-unit cell. The pattern is dominated by a strong meridional reflection at 4.82 Å, which corresponds to the (020) planes of the γ-form[2]. Much weaker reflections at 4.41 Å (110_γ) and 4.28 Å (021_γ) are also perceptible, although their exact azimuthal disposition is not clear. Were it not for the infra-red evidence[7,14], this electron-diffraction pattern alone could not unequivocally establish the presence of γ-PVF$_2$, because its three reflections could also arise from a mixture of α- and β-crystals. However, in conjunction with the i.r. results, it shows that the transformation does not alter the initial orientation of the spherulite, in which the *b*-axis is radial[10]. Thus, the transformation can proceed along the molecular stems without disturbing their relative positions since both the dimensions and the radial orientation of the *ab* cell base remain the same regardless of whether these crystals are in the α- or γ-phase.

The above describe morphologically the most general type of crystalline transformation in α-PVF$_2$. Evidence for transformations originating at the periphery can also be seen in the published micrographs of Gianotti *et al.*[6] and Prest and Luca[7], although no explicit reference to such transformations is made in these papers. However, the latter authors[7] describe α→γ transformations originating at the nuclei of some α-spherulites at very high temperatures (162°C and above) and advancing outwards. These transformations have also been seen here, and are identical in nature to those initiated at the periphery of α-spherulites. They may be considered a special case of the general phenomenon described above: with increasing temperature, sufficient energy is provided for overcoming the activation barrier to transformation at special points not in contact with mixed spherulites; nuclei are, of course, such special points, particularly when they are heterogeneous. 162°C is the temperature at which transformations initiated at both the peripheries and the nuclei of some α-spherulites are seen with some frequency (see also Fig. 4 of ref. 14). As temperature is increased above 162°C, transformations originating at α-nuclei gain in relative prominence for two reasons: (1) added thermal energy is available, so that the activation barrier is overcome at more α-nuclei; and (2) because of very low nucleation and growth rates, the average time required for α- and mixed spherulites to meet and initiate a transformation at their boundaries is extremely long.

Having examined the morphological aspects of solid state transformations in α-PVF$_2$, we may now consider their growth rates. 'Growth rate' in this sense is defined as the rate of advance of the tips of high-melting lamellae (towards or away from the nucleus) as a function of time. The data are presented in *Figure* 5, where the abscissa measures the time elapsed from the instant that the oven was brought to the selected crystallization temperature. At first, the radial length of transformed regions was measured after melting out the remaining (i.e. untransformed) α-lamellae; fresh samples had to be used for each

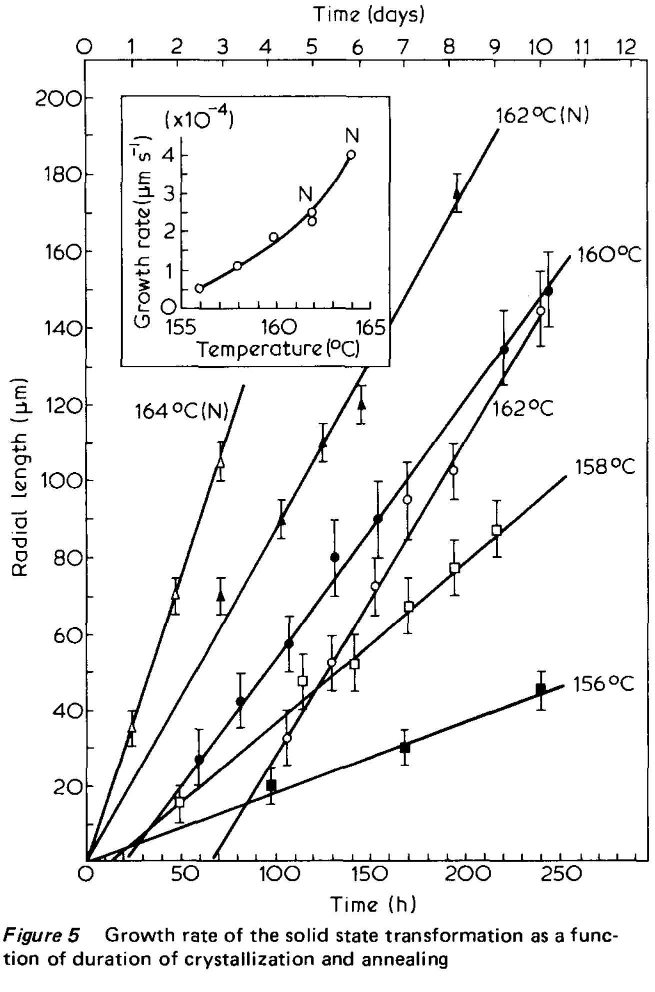

Figure 5 Growth rate of the solid state transformation as a function of duration of crystallization and annealing

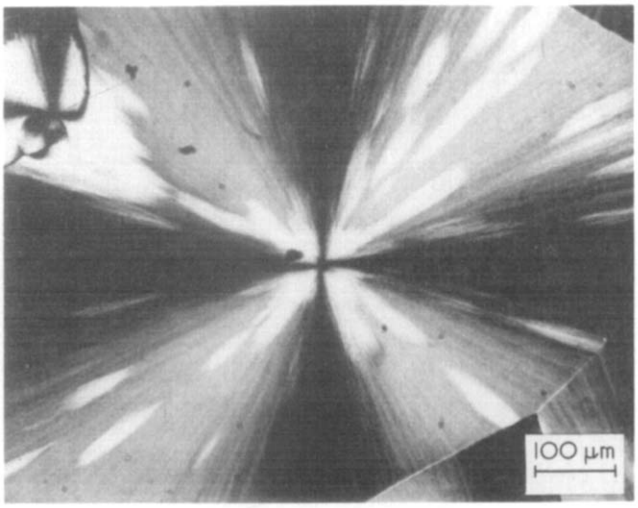

Figure 6 Appearance of a sample annealed at very high temperature. The specimen was crystallized at 156°C for 9 days and annealed at 165°C for 2 days. $T_{\text{photo}} = 172°\text{C}$

datum point. Because this technique involves an extremely long cumulative time, an alternative procedure (which is not destructive to the spherulitic morphology) was ultimately used. As is described separately[14], it was discovered that this crystalline transformation is accompanied by preferential thermal degradation of the transformed regions. These regions become perceptibly discoloured, so that their radial lengths could easily be measured *in situ* by use of an ocular micrometer without interruption of the thermal treatment. By melting of some test specimens (see also Fig. 4 of ref. 14) it was ascertained that the radial length of the high temperature survivors is identical to that of the degraded areas, so that no error was introduced by use of this technique.

Curves of radial length *versus* time at the indicated temperatures are seen in *Figure* 5. Each datum bar represents the spread in values among 5–10 measurements taken from the first spherulites to transform. The spread can be quite large: as is seen, for example, in *Figure 2b*, the outlines of the growing transformation fronts are very jagged and uneven for both those originating at the periphery and at the nucleus. In addition, the length of transformed regions advancing towards the centre depends upon the position of initiating mixed spherulites relative to the α-nucleus: when these are close to the nucleus, the transformation will be initiated sooner (and the resulting radial lengths will be greater) than when mixed spherulites are farther away (see also *Figure 2a*). In spite of the spread in individual data points, the growth rates of the transformation appear to be clearly linear. This indicates that although degradation takes place simultaneously with the change in molecular conformation of α-type chains, it has no controlling effect on growth rate of the transformation, as it does for example in crystallization from the melt[15]. The overall growth rate is extremely slow (or the order of 10^{-4} $\mu\text{m s}^{-1}$) and increases with temperature. Very good agreement is seen for the 162°C lines representing initiation at the nucleus (N) and at the periphery, further establishing the identical nature of these two phenomena. It is interesting to note that the first of these lines passes through the origin, as does the 164°C line, implying that transformation began essentially immediately after crystallization. The intercepts of all other growth-rate lines with the abscissa provide only a general indication of when transformation must have started in the particular spherulites studied, and reflect the longer time required for contact between the two spherulitic forms at higher temperatures.

The results discussed so far describe the incidence of crystalline transformations in samples both crystallized and annealed at the same high temperature. This phenomenon has also been investigated in samples originally crystallized at one temperature and then annealed at another. Generally, when a sample is crystallizing in the high-temperature region, the transformation appears to adapt to changes in temperature. Depending upon its magnitude, a drop in temperature retards or terminates growth of transformed regions. Similarly, a rise in temperature brings about increases in the rate of transformation and, if high enough, induces new transformations about some α-nuclei; many α-nuclei, however, remain passive even at the highest temperatures. At the same time, some α-spherulites undergo transformations at multiple points in their interiors when the temperature is raised to 165°C or above. This is illustrated in *Figure* 6, where an α-spherulite had crystallized at 156°C prior to annealing at 165°C. The typical transformation initiated by the mixed spherulite at the crystallization temperature

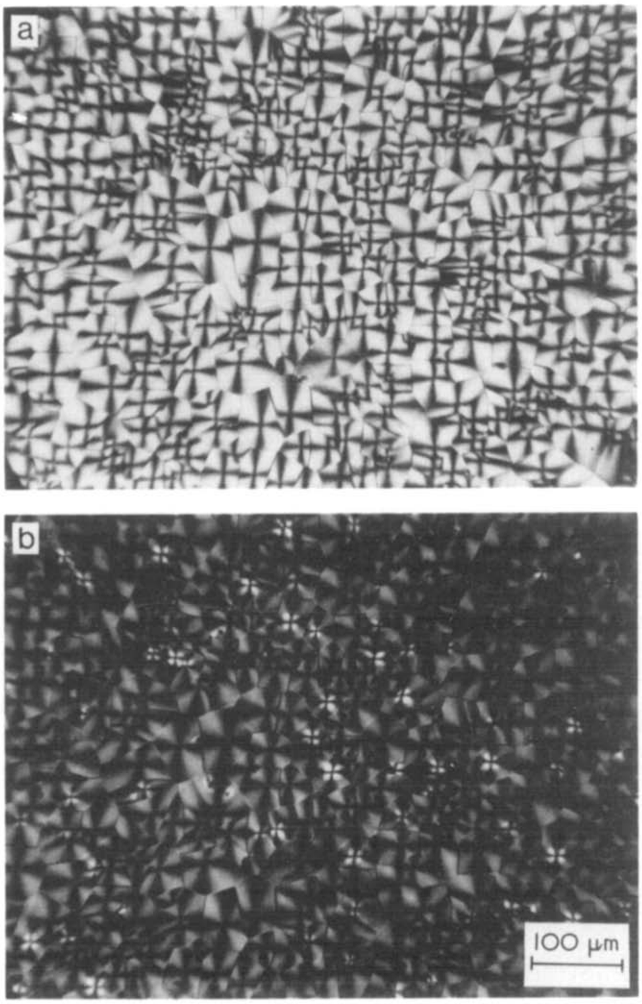

Figure 7 (a) Typical appearance of a sample crystallized at low temperature. $T_c = 145°\text{C}$, $t = 1/2$ h. (b) The same sample after annealing at 160°C for 95 h; $T_{\text{photo}} = 169°\text{C}$

is seen in the upper left-hand corner; the narrow regions of high-melting crystals dispersed throughout the spherulite, as well as the transformation about the nucleus, appeared after the rise in temperature.

Let us finally examine what happens at the lower end of the temperature spectrum. As has been mentioned earlier, transformations are seen at all temperatures in which mixed spherulites are grown. However, as the temperature drops below ~156°C, the incidence and extent of such transformations become very limited. This is primarily due to early nucleation and fast growth of α-spherulites, and the consequent scarcity of their mixed counterparts; furthermore, owing to the diminished thermal energy available for transformations, growth rates are very low (see also *Figure* 5). Samples crystallized under ~152°C generally consist entirely of α-spherulites[7,8] and yield no high-melting phase even after prolonged residence at the crystallization temperature. In such specimens, very limited transformations are seen after large increases in temperature: for example, after 95 h at 160°C, the sample of *Figure* 7, originally crystallized at 145°C, shows only minimal transformation about a small fraction of its α-nuclei.

CONCLUSIONS

A solid-state transformation in α-spherulites of PVF_2 occurs at high temperatures and yields the high-melting γ-phase. At all but the highest temperatures, this transformation is initiated by mixed spherulites at the peripheries of their α-counterparts; from there, the transformation advances towards the nuclei of α-spherulites at a linear growth rate along their lamellae, and at a much lower rate across them. As the temperature is increased, both the growth rate of the transformation and the average initiation time from the periphery of α-spherulites also increase; in addition, transformations initiated at the nucleus begin to occur with some frequency. When samples are annealed at very high temperatures, a few spherulites exhibit irregularly distributed regions of the high-melting phase. On the other hand, in samples crystallized below ~152°C, the transformation is very limited, even after prolonged subsequent annealing at high temperatures.

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