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Morphology and phase transition of high melt temperature crystallized poly(vinylidene fluoride)

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When PVDF is crystallized at temperatures above 155 °C it presents a multiform morphology composed of ringed, non ringed and mixed spherulites. Infrared spectroscopy showed that the ringed spherulites are formed exclusively by the α phase when crystallization takes place at temperatures below 155 °C. Higher temperatures induce a solid-state $\alpha \rightarrow \gamma$ phase transformation in these structures, increasing the amount of γ phase with crystallization time. The rate at which this transformation takes place increases with crystallization temperature. The non ringed spherulites, only formed at crystallization temperatures above 155 °C, consist predominantly of the γ phase, crystallized from the melt, with small α phase inclusions. The melt process of the different spherulites, observed by optical microscopy and calorimetric measurements (DSC) showed that the melt temperature of the γ phase, originated from the phase transition, is 8 °C higher than that crystallized directly from the melt. Optical micrographs of samples heated up to 186 °C and quickly cooled allowed visualization of the ringed spherulite regions which underwent the $\alpha \rightarrow \gamma$ phase transformation at different crystallization times and temperatures. © *2000 Kluwer Academic Publishers*

1. Introduction

Due to its important pyro and piezoelectric properties, poly(vinylidene fluoride) (PVDF) has been widely investigated since 1970. Besides these properties PVDF also exhibits at least four crystalline phases, known as α, β, γ and δ. The apolar α phase predominates at melt crystallization below 160 °C. The oriented polar β phase is normally obtained by drawing of α phase films at temperatures between 70 and 100 °C. The unoriented β phase may be obtained by crystallization from dimethylformamide (DMF) or dimethyl acetamide (DMA) solutions at temperatures below 70 °C [1]. Higher temperatures result in a mixture of the α and β phases, with the α fraction increasing with temperature increase. The polar γ phase may be obtained from both solution and melt crystallization at temperatures above 160 °C or by annealing α phase samples between 175 and 185 °C [1–4]. The δ phase, a polar version of the α phase, may be obtained by polarizing the α phase at high electric fields [5]. In virtue of this polymorphism, very uncommon in polymer materials, PVDF presents a very varied morphology that strongly depends on crystallization temperature and time. The first investigations relating morphology to crystallization time and temperature of PVDF were performed by Gianotti and coworkers [6] and by Prest and Luca [3]. Both groups observed, through optical polarized light microscopy, that crystallization above 150 °C produces two distinct spherulite forms: some large highly birefringent presenting closely spaced concentric rings and others smaller less birefringent exhibiting a coarser ringed texture than their larger neighbors. By following the melt process of a sample crystallized at 162 °C, Prest and Luca [3] observed that the birefringence of several, but not all, large spherulites would start disappearing at 172 °C. Some of these structures maintained their birefringence partially invariant above this temperature, remaining normally the center and an aureole. The smaller spherulites started losing their birefringence at 178 °C and the remaining large ones at 186 °C. Thermal analysis (DSC) showed the appearance of three endotherms for samples crystallized above 152 °C, which after infrared spectroscopy (IRS) analysis, the authors attributed to fusion of the α, β and γ phases, in increasing order of temperature. The authors assumed that during crystallization nucleation and growth of the α and β phases took place, forming, respectively, the larger thin ringed spherulites and the smaller coarse ringed ones. Given enough time a solid-state $\alpha \rightarrow \gamma$ phase transformation would take place, without modification of the appearance of the larger spherulites, when observed by optical microscopy. This transformation initiates at the center of the spherulite and propagates radially throughout the structure. Osaki and Ishida [2] also suggested such transformation on investigating annealing and isothermal crystallization of PVDF at elevated temperatures. In a posterior morphological investigation Lovinger [7] demonstrated that the smaller spherulites were in fact formed by a structure compatible with that of the γ phase, as suggested by

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Gianotti and coworkers [6], with small inclusions probably from the α phase, a result afterwards confirmed by Morra and Stain [8]. Lovinger [7] also observed that at the region where the different spherulites meet the $\alpha \rightarrow \gamma$ transformation suggested by Prest and Lucas preferentially starts at the edges of the ringed spherulites, where their lamellae are intermingled with those of the smaller ones. With increase in crystallization temperature this transformation may also initiate at the center of the larger spherulites and then propagate radially. Lovinger [4], showed that the growth rate of the larger spherulites surpasses that of the smaller ones up to a certain crystallization temperature, above which the process inverts. Both this temperature and the temperature at which the small spherulites start taking shape depend on the resin used. The concentric rings exhibited by the large spherulites become more spaced with increase in crystallization temperature. Takahashi and coworkers [9] proposed possible solid-state $\alpha \rightarrow \gamma$ transformation mechanisms. Posterior works [10, 11] showed that application of intense electric fields ($E > 70$ kV/cm) may increase the γ phase nucleation rate.

The scope of the current investigation was to obtain evidence that corroborate the conclusions obtained in previous works on the crystalline phases present in the different types of spherulites, by means of a systematic study of the isothermal crystallization of PVDF from the melt at elevated temperatures. We also endeavored to verify the dependence of the solid-state $\alpha \rightarrow \gamma$ transformation process on crystallization time and temperature and to suggest a possible cause for the existence of ringed spherulites at the center and non ringed at the edges, observed at high temperature crystallization of PVDF [1] or in PVDF/PMMA blends [8].

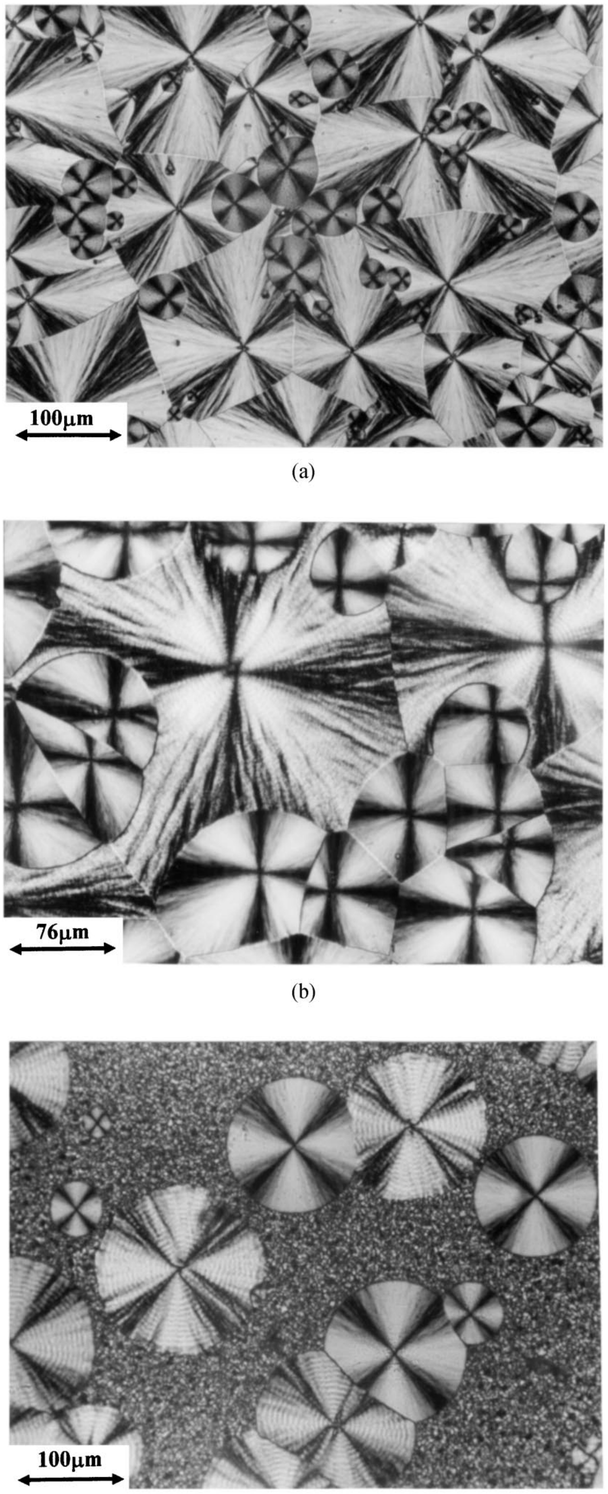
2. Experimental

Films between 10 and 15 μm were obtained by spreading a solution of PVDF in DMF on a glass substrate. The initial concentration of the solution was 20 wt % PVDF (FORAFLON® F4000HD, Atochem) and the solvent was evaporated at 110 °C for 30 min inside a closed hood with exhaustion. Next, the films were cooled to room temperature (25 °C) and easily removed from the substrate. IR spectra and polarized light optical microscopy showed that the films presented predominantly the α phase and a morphology composed of very small spherulites, respectively, in agreement with results obtained in a previous work [1]. Circular specimens with diameter of 12 mm were cut from these films, maintained under a glass lamina on a hot stage (THMS 600, Linkan) at 230 °C for 10 min, and subsequently cooled (40 °C/min) down to the desired crystallization temperature at which they were kept for different times and then cooled to room temperature. The crystallization temperatures used varied from 160 to 168 °C. The whole process was accompanied by a polarized light optical microscope (DMRXP, Leica) attached to a VCR and a 35 mm photographic camera with automatic exposure control. Identification of the crystalline phase(s) present in each spherulite was performed at room temperature by means of an FTIR spectrometer (Magna 550, Nicolet) connected to an optical microscope (IR-Plan) which allowed to obtain spectra in the range between 1000 and 700 cm^{-1} of a minimum circular sample area of 20 μm. Calorimetric measurements were carried out in a Perkin Elmer DSC-7 at a heating rate of 10 °C/min.

3. Results and discussion

Micrographs of the samples crystallized for 24 h at three different temperatures are shown in Fig. 1. The sample crystallized at 160 °C (Fig. 1a) presented a morphology very similar to that observed by Prest and Luca [3], consisting of two different size spherulites. However, in contrast to that described by the authors, the smaller spherulites did not present a coarser ringed texture than the larger ones. A closer look showed that while the larger spherulites present closely spaced concentric rings, the smaller ones are not ringed, as shown in Fig. 2, an amplified detail of the two types of spherulites present in the sample of Fig. 1a. In this work we will denominate the two different types ringed and non ringed. As already observed in a previous work [12], using FORAFLON® F4000HD resin the non ringed spherulites start forming in melt crystallization only at $T \geq 155$ °C. With temperature increase the nucleation rate of the ringed spherulites decreases, resulting in larger spherulites and allowing an increase in the number and size of the non ringed ones. The growth rate of the ringed spherulites surpasses that of the non ringed ones only below 168 °C, after which the process inverts. As a result, at 168 °C the average diameters of the two types of spherulites are very similar (Fig. 1c). At this temperature the growth rate of these spherulites were so low that complete crystallization of the sample at 24 h could not be accomplished, resulting in regions with very small spherulites, crystallized during cooling. Fig. 1a–c also shows how the distance between the concentric rings of the ringed spherulites increases with crystallization temperature, a phenomenon already observed by Lovinger [4]. Some samples crystallized at $T \geq 165$ °C presented non ringed spherulites with very irregular birefringence, as can be seen in Fig. 3.

In order to check the predominating crystalline phase in each spherulite type, IR spectra were obtained of several ringed and non ringed spherulites in all samples. The ringed spherulites were seen to present different spectra, which could be classified in four representative types, shown in Fig. 4. Analysis of the characteristic absorption bands of the α phase (766, 795, 855 and 976 cm^{-1}) and the γ phase (778, 812, 834 and 840 cm^{-1}) shows that the spectra, indicated in the figure by the letters a, b, c and d, have different fractions of α and γ phases which were arranged in increasing order of the γ phase present. The ringed spherulites may, thus, contain predominantly the α phase or a mixture of the α and γ phases with different proportions of each one. All ringed spherulites from the samples crystallized at 160 °C during times shorter than 16 h presented spectra similar to that of Fig. 4a, i.e., with complete predominance of the α phase. With



(a)

(b)

(c)

Figure 1 Morphologies presented by the samples crystallized during 24 h: (a) 160, (b) 165 and (c) 168 °C.

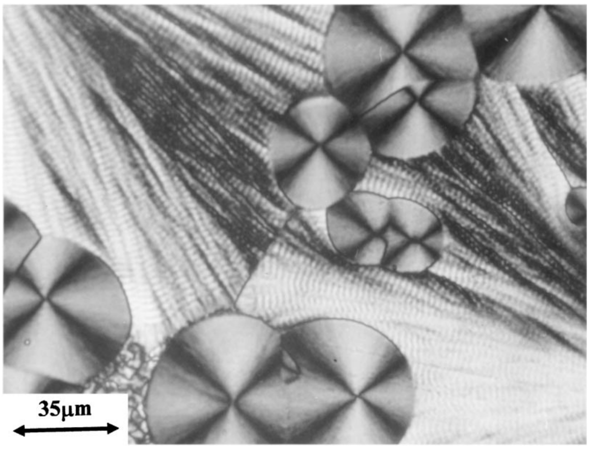


Figure 2 Amplified detail of the different spherulites present in the sample crystallized at 160 °C for 24 h.

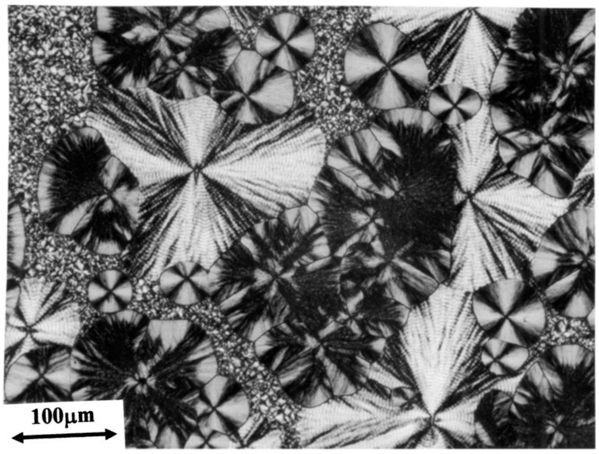


Figure 3 Morphologies presented by some samples crystallized at 165 °C, where some non ringed spherulites with irregular birefringence can be seen.

increase in crystallization time the number of ringed spherulites that yielded spectra indicating the presence of a small amount of the γ phase increased, as that shown in Fig. 4b. The spectra of the major part of ringed spherulites crystallized at 165 °C for more than 8 h showed the presence of the γ phase and the amount of this phase increased with crystallization time. However, even some of the ringed spherulites from samples crystallized for 48 h yielded spectra showing complete predominance of the α phase. The samples crystallized at 168 °C presented the γ phase in almost all the ringed spherulites and the amount of this phase increased with crystallization time. These results indicate that the fraction of the γ phase that forms in most of the ringed spherulites, probably through the solid-state $\alpha \rightarrow \gamma$ transformation suggested by Prest and Luca [3], increases with crystallization time and the rate at which transformation occurs increases with temperature. It is interesting to note that optical microscopy does not distinguish, in a ringed spherulite, between the region that has already undergone the $\alpha \rightarrow \gamma$ transformation and that which still remains in the α phase.

A different behavior was observed for the non ringed spherulites. All presented very similar spectra, regardless of crystallization time. A representative spectrum is presented in Fig. 5, showing a mixture of the α and γ phase, with predominance of the latter. With increase in crystallization temperature a slight increase in γ fraction is observed in some of these spherulites. These results indicate that the non ringed spherulites formed predominantly by the γ phase nucleate and grow in the crystallization process, without phase transformation in the course of time. Small α phase inclusions exist in these spherulites, whose amount slightly decreases with increase in crystallization temperature.

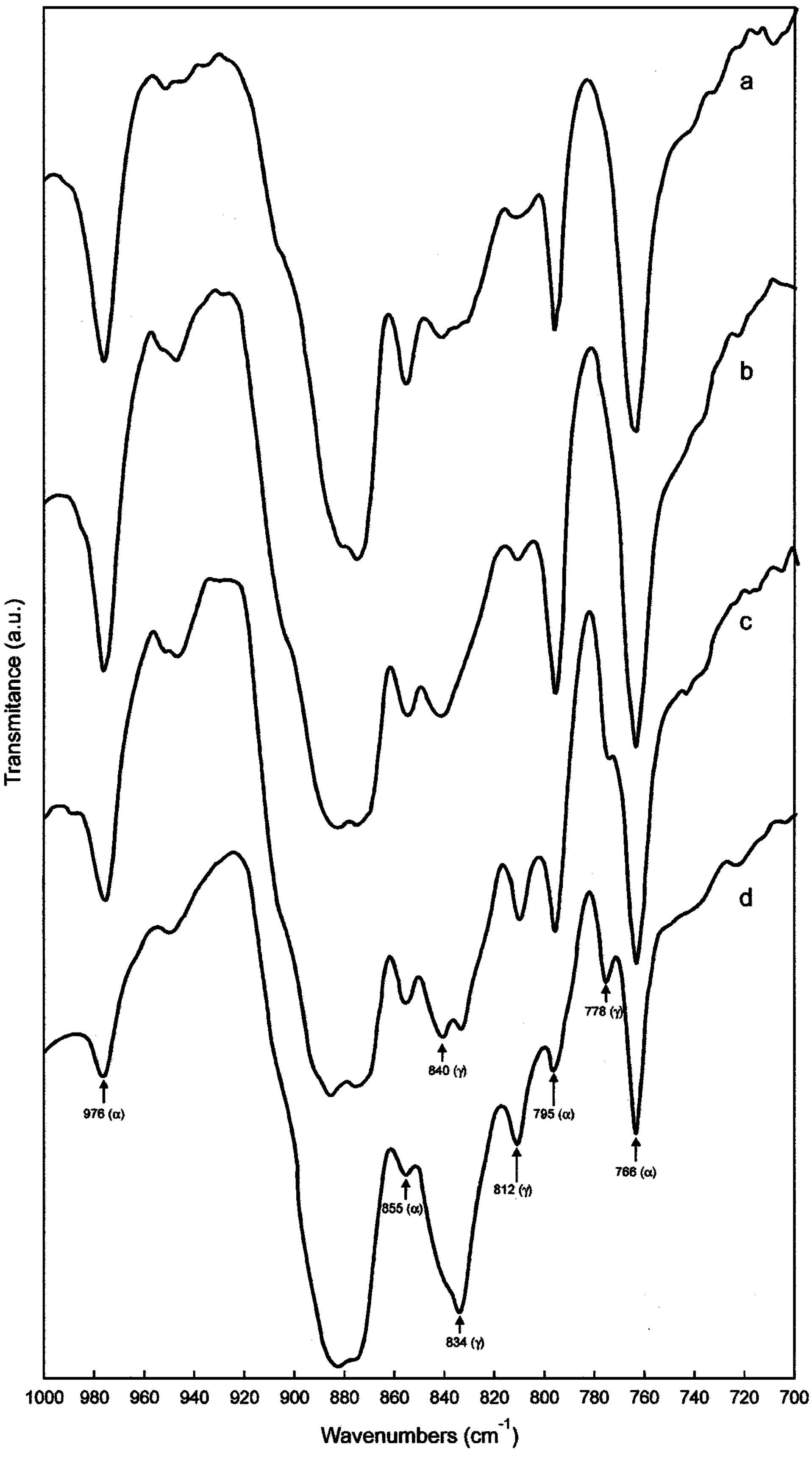


Figure 4 Some infrared spectra presented by the ringed spherulites. The arrows indicate the characteristic absorption frequencies of the α and γ phases.

In order to investigate the behavior of different spherulites during fusion, samples crystallized at different times and temperatures were heated at a rate of 3 °C/min from room temperature to 230 °C. The whole process was accompanied by polarized light optical microscopy and some stages were photographed. Fig. 6 shows the micrograph of the sample crystallized at 160 °C for 24 h (the same of Fig. 1a) after being

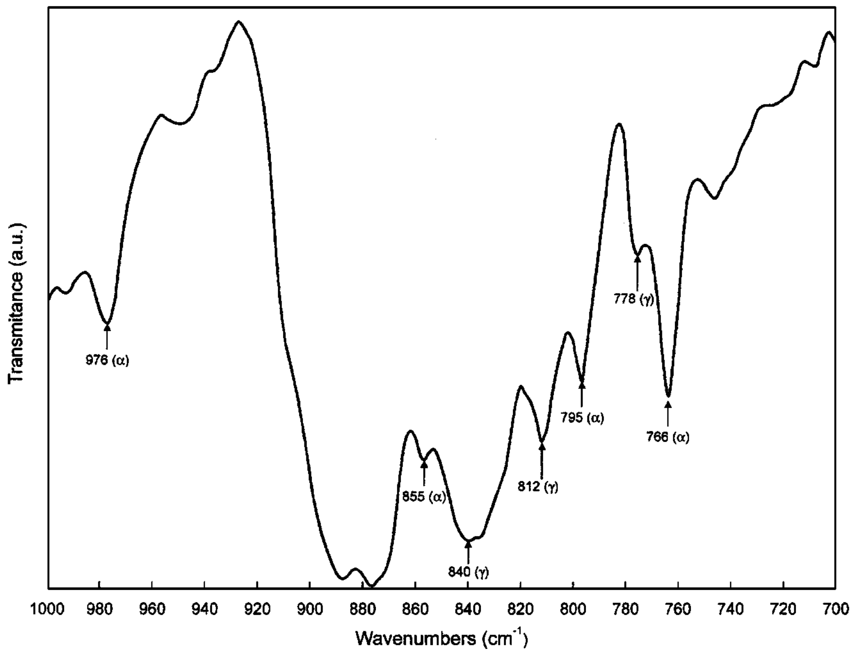


Figure 5 A typical IR spectrum of non ringed spherulite.

heated to 179 °C. All ringed spherulites lose birefringence between 171 and 175 °C, remaining only small regions bordering the non ringed spherulites and sporadically small central regions. At 180 °C the non ringed spherulites start losing birefringence, which disappears completely at 184 °C. Above this temperature only the small ringed regions remain, losing birefringence between 188 and 193 °C. This result is very similar to that of Morra and Stein [7] and Lovinger [8], using Kynar (Pennwalt Corp.) resin. This behavior is affected by the crystallization time. In the sample crystallized at 160 °C for 4 h all ringed spherulites lost birefringence completely at 175 °C. With increase in crystallization time there is an increase in the ringed spherulites adjacent to the non ringed ones that remained after this temperature, as well as the central region of these spherulites. With increase in temperature, for the same crystallization time, there is an increase in the ringed spherulite regions that maintain birefringence up to 193 °C.

All micrographs obtained at elevated temperatures during the melt process showed to lack clearness, as that shown in Fig. 6, probably due to the moving air between the sample and the microscope's objective during exposure (average exposure time for these photos was 45 s). In order to visualize more clearly the regions of the ringed spherulites that only lose birefringence above 192 °C, i.e., the regions where the $\alpha \rightarrow \gamma$ phase transformation had already occurred, the samples were heated to a given temperature and subsequently quickly cooled (50 °C/min) to room temperature. In this way the structures that remained birefringent up to that temperature could be photographed at room temperature. Fig. 7 presents a micrograph of the sample crystallized at 160 °C for 24 h after being heated to 179 °C and quickly cooled to room temperature. One may note the resemblance between this figure and Fig. 6, since it is the same sample (another region) in similar conditions. The only difference is

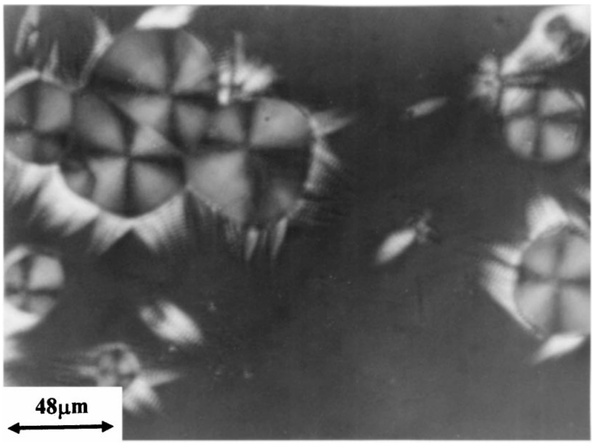


Figure 6 Micrograph observed at 179 °C after heating a sample crystallized at 160 °C for 24 h.

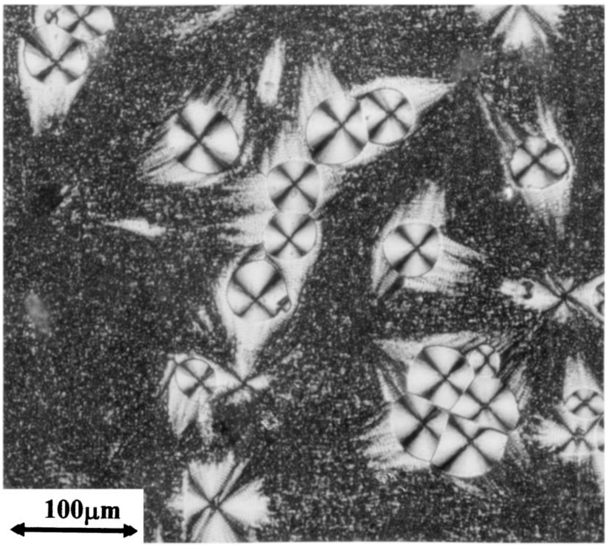


Figure 7 Micrograph obtained at room temperature of a sample crystallized at 160 °C for 24 h, after being heated to 179 °C and quickly cooled.

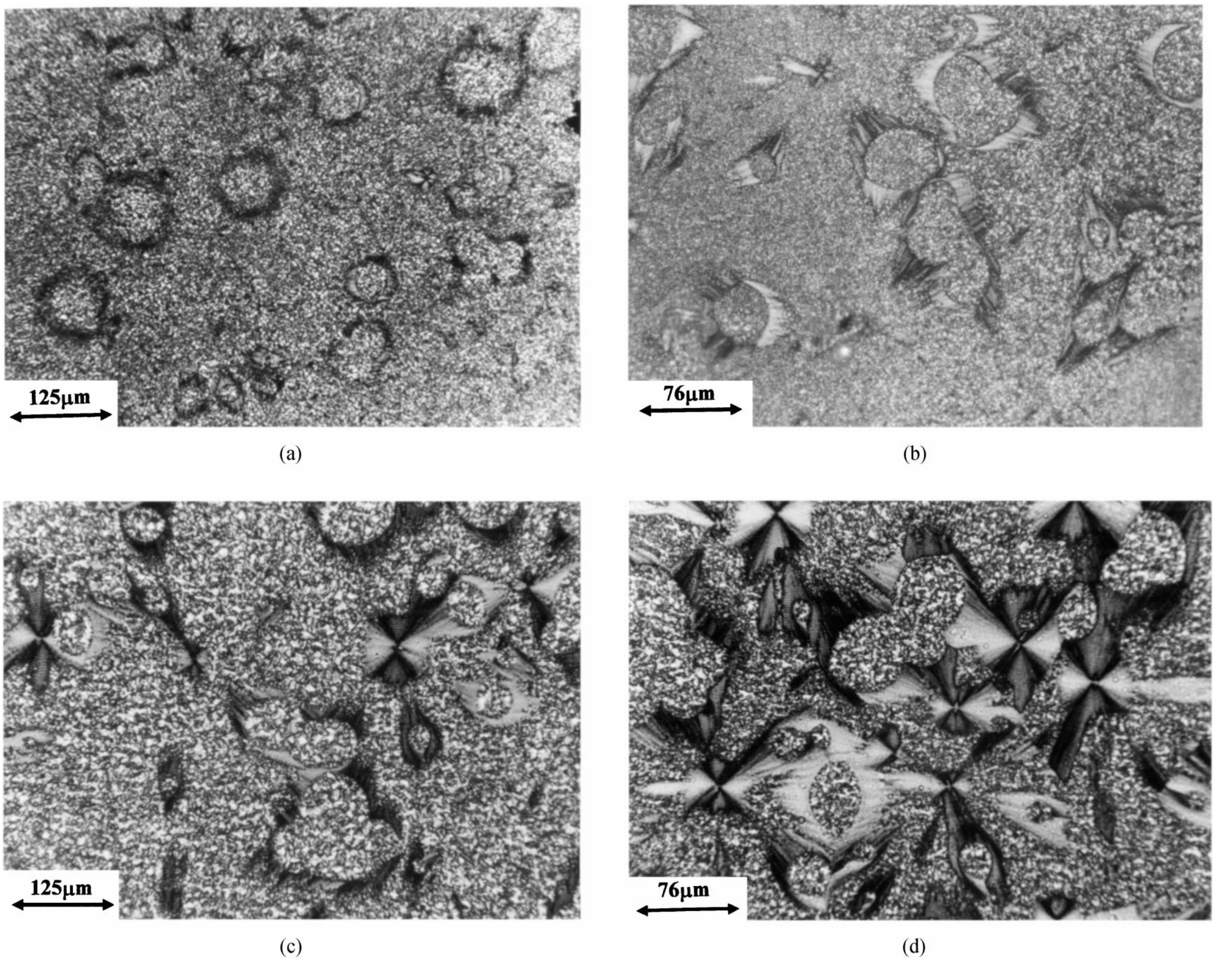
that the sample photographed at room temperature presents instead of the dark melted region very small spherulites formed during cooling, however the enhanced clearness allows better visualization of details.

All samples were heated to 186 °C and quenched to room temperature. At 186 °C the part of ringed spherulites that loses birefringence between 171 and 175 °C and all non ringed spherulites have already disappeared, remaining only the regions of the ringed spherulites that melt at higher temperature. These regions were photographed at room temperature for the samples crystallized during different times and temperatures. Fig. 8 shows the results obtained for the samples crystallized at 160 °C for 8, 16, 24 and 48 h. It can be seen that in the sample crystallized for 8 h only small regions of the ringed spherulites remained at the borders between these and the non ringed ones. These regions propagate with crystallization time towards the center of the spherulites (Fig. 8b). In some cases the birefringence of the central regions of the spherulites remain unaltered, which propagate radially with crystallization time (Fig. 8b and c). As already observed, the regions of the ringed spherulites that underwent phase transformation increases with crystallization time.

Fig. 9 shows the regions of ringed spherulites that remained after heating to 186 °C for the sample crystallized at 165 °C for 16 h. A micrograph of lower amplification is presented in order to enable observation of a larger sample area (9a), as well as two others showing details of the first with different amplifications (9b and c). In this case some ringed spherulites are seen to remain practically intact at 186 °C (Fig. 9a) showing that the $\alpha \rightarrow \gamma$ transformation has occurred in almost their complete extent. In others, the regions that remained in the α phase melted between 171 and 175 °C, resulting in partially destroyed structures as those evidenced in Fig. 9b and c. It can also be seen that regions of ringed spherulites that remained in this sample were larger than those in the sample crystallized for 16 h at 160 °C (Fig. 8b), confirming that the rate at which the phase transformations takes place increases with crystallization temperature.

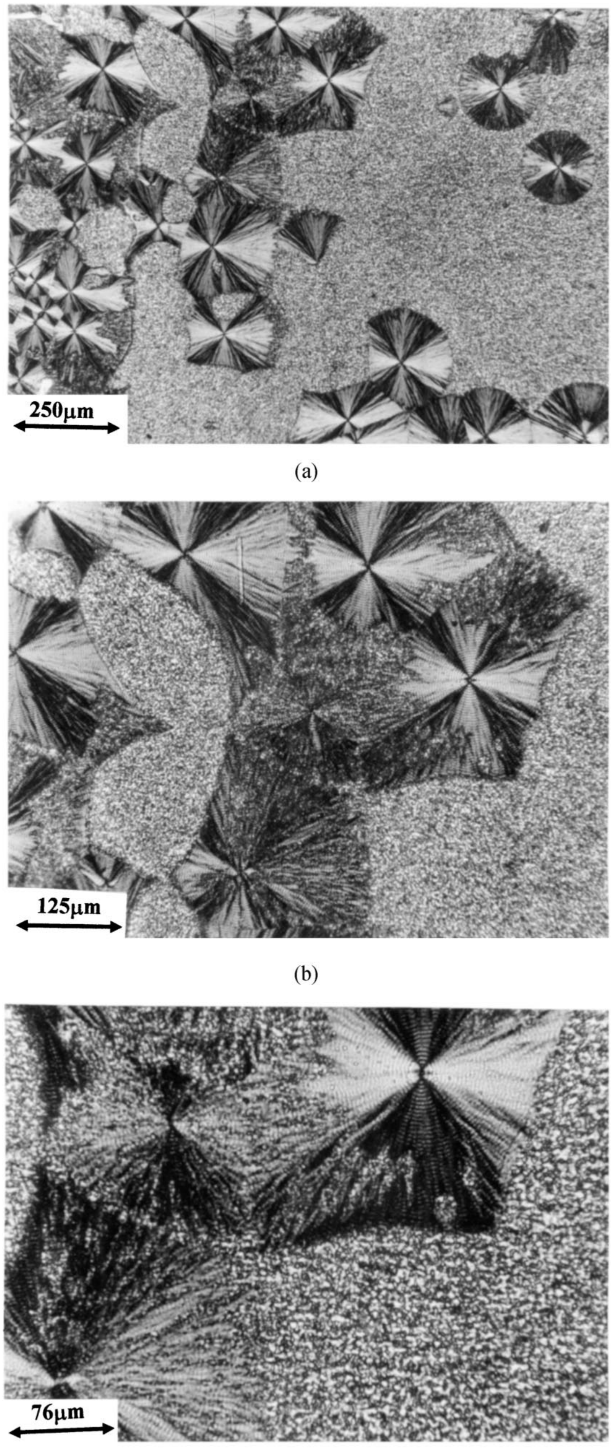
In the samples crystallized at 168 °C for 16 h almost all ringed spherulites apparently remained intact after heating at 186 °C and subsequent cooling, as shown in Fig. 10. However, IR spectra obtained of these spherulites at room temperature showed to be similar to those presented in Fig. 4d, demonstrating a predominance of the γ phase, however still with small α phase inclusions.

Thermal analysis (DSC) was carried out in all samples and Fig. 11 shows the DSC curves obtained of samples crystallized for 24 h at 160, 165 and 168 °C. In the sample crystallized at 160 °C three endotherms



(a) (b)
(c) (d)

Figure 8 Micrographs obtained at room temperature of samples crystallized at 160 °C for (a) 8, (b) 16, (c) 24 h and (d) 48 h, after being heated to 186 °C and quickly cooled.



(a)

(b)

(c)

Figure 9 (a) Micrograph obtained at room temperature of a sample crystallized at 165 °C for 16 h, after being heated to 186 °C and quickly cooled. (b) and (c) details of the micrograph with different amplifications.

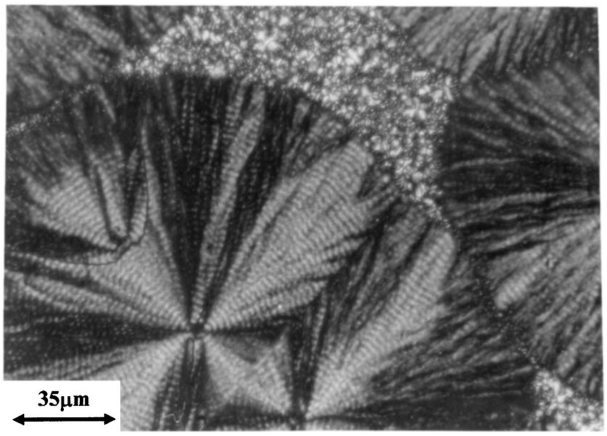


Figure 10 Micrograph obtained at room temperature of a sample crystallized at 168 °C for 16 h, after being heated to 186 °C and quickly cooled.

are evident with peaks at approximately 169, 177 and 185 °C. The lower temperature endotherm is likely associated with fusion of the ringed spherulites that crystallize at 160 °C in the α phase and which do not undergo transformation into the γ phase, since, as observed in optical microscopy, they lose birefringence between 171 and 175 °C. The endotherm with maximum at 177 °C is likely related to the fusion of the non ringed spherulites composed predominantly of the γ phase, whose birefringence disappears between 180 and 184 °C. Finally, the high temperature endotherm (185 °C) is likely associated with the fusion of the ringed spherulite regions composed of the γ phase, originated from the $\alpha \rightarrow \gamma$ transformation, whose birefringence disappears only between 188 and 193 °C. With increase in crystallization time, for a same temperature, the area of the 185 °C endotherm is seen to increase with a corresponding reduction in that at 169 °C, showing that the γ phase in the ringed spherulites is formed by the $\alpha \rightarrow \gamma$ transformation.

In the sample crystallized at 165 °C the same three endotherms can be observed, slightly shifted towards higher temperatures (maxima at approximately 171, 178 and 187 °C). This shift was expected, since T_m increases with crystallization temperature for both crystalline phases. One may also note a strong reduction in the 169 °C endotherm and an increase in the 185 °C one, when compared to those obtained of the sample crystallized at 160 °C. This result confirms the increase in the $\alpha \rightarrow \gamma$ transformation rate with increasing crystallization temperature.

The DSC curve of the sample crystallized at 168 °C also exhibits three endotherms peaking at around 167, 180 and 188 °C. The lower temperature endotherm likely corresponds to the fusion of the very small spherulites crystallized during cooling. Indeed, this endotherm does not appear in the samples crystallized at 160 and 165 °C, as they crystallized completely during the 24 h. On the other hand, in this case the endotherm corresponding to the fusion of the ringed spherulites crystallized at 168 °C, and which did not undergo the $\alpha \rightarrow \gamma$ phase transformation, is not observed. This result indicates that the 24 h were sufficient for the transformation to occur in practically all the ringed spherulites, which agrees with our observation by optical microscopy.

Some samples crystallized at 168 °C presented some ringed spherulites in the center and non ringed at the edges, as shown in Fig. 12. A possible explanation for the formation of such spherulites is that at this elevated temperature the $\alpha \rightarrow \gamma$ phase transformation propagates in the spherulite, from the center towards the edges, at a higher rate than the growth rate. When the $\alpha \rightarrow \gamma$ transition front reaches the growth front of

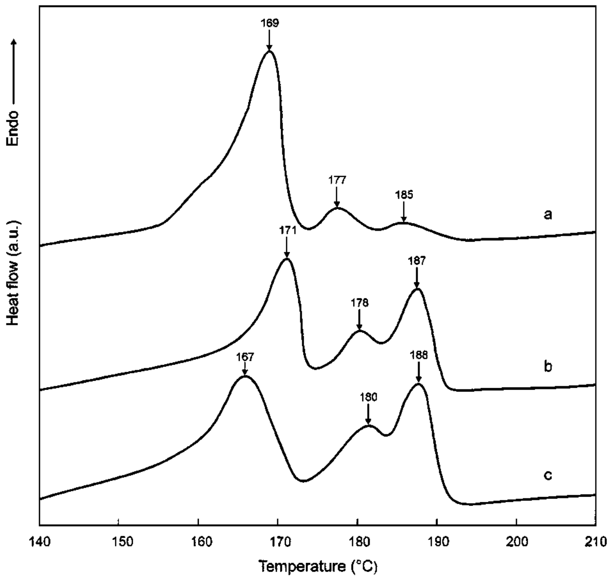


Figure 11 DSC curves of the samples crystallized during 24 h at (a) 160, (b) 165 and (c) 168 °C.

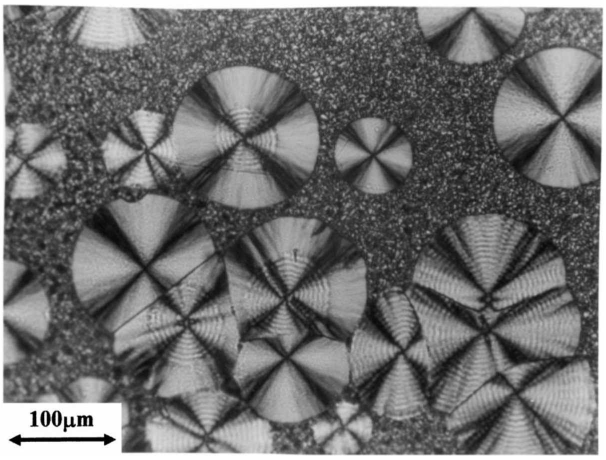


Figure 12 Micrograph of a sample crystallized at 168 °C for 24 h, showing the occurrence of ringed spherulites in the center and non ringed spherulites at the borders.

the α spherulites, these proceed to grow in the γ form, resulting in the non ringed border of the spherulites. Indeed, in the heating process, the non ringed border of these spherulites loses birefringence between 180 and 184 °C (like the non ringed) and the internal region between 189 and 194 °C.

It is interesting to note that the same crystalline phase may present two distinct melt temperatures. The γ phase crystallized from the melt presents a T_m about 8 °C lower than that formed from the solid-state $\alpha \rightarrow \gamma$ transformation. This probably happens because the transformation takes place in an annealing process and the crystals so formed are supposed to be more organized than those directly crystallized in the γ phase. The reason why the α phase spherulites are ringed and the predominantly γ phase ones are not is still unknown.

4. Conclusion

PVDF when crystallized from the melt at temperatures above 155 °C presents a morphology composed of two types of spherulites: ringed and non ringed. The ringed ones consist predominantly of the α phase crystallized directly from the melt. With crystallization time an $\alpha \rightarrow \gamma$ solid-state phase transformation takes place, whose rate increases with temperature. The non ringed spherulites are predominantly formed by the γ phase, which crystallizes from the melt, with small α phase inclusions. The γ phase formed from the phase transformation has a T_m about 8 °C higher than that of the same phase formed directly from the melt. Some samples crystallized at 168 °C result in ringed spherulites in the center and non ringed at the borders, possibly due to higher rate at which the phase transformation propagates compared to the growth rate.

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