Influence of the Crystallization Kinetics on the Microstructural Properties of γ-PVDF

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Abstract

The kinetics of the isothermal crystallization of the γ-phase Poly(vinylidene fluoride) has been investigated. Samples were prepared from the melt at different crystallisation temperatures and the variation of the microstructure of the samples was monitored with time by optical microscopy. Raman and Infrared transmission spectroscopies also show the appearance of the γ-phase for higher crystallisation temperatures. Two types of γ-phase spherulites have

been identified. These spherulites represents different ways to obtain the γ-phase and show different thermal stability. The correlation between microstructure and kinetic parameters allows the tailoring of the microstructure by choosing the crystallisation conditions of the samples.

Introduction

Poly(vinylidene fluoride) (PVDF) is the main representative of a family of polymeric materials with high interesting scientific and technological properties. This polymer is known for its outstanding electroactive properties, non-linear optical susceptibility and an unusually high dielectric constant among polymers [1]. The electroactive properties heavily depend on the phase content, microstructure and degree of crystallinity of the samples, which in turn depend on the processing conditions. In particular the microstructure of α-PVDF plays an important role in the α - to β transformation by stretching [2,3]. This stretching process is the typical way for obtaining the most common electroactive polymorph [3, 4] and deeply influences on the properties of the electroactive β-phase [5]. Due to the technological interest the α - and β-phase have been and still are deeply studied. Nevertheless, PVDF still show at least two further polymorphs: the γ and δ phases. The γ phase shows polymeric chains in an arrangement $T_3CT_3C^-$, with a polar monoclinic unit cell and space group C2m [1]. It has been reported that two types of gamma phase can coexist in the same sample [6].

In the present work, the kinetics and microestructural changes of the isothermal crystallization from the melt at different crystallisation temperatures, leading to the γ -phase of PVDF has been studied. Spectroscopic and DSC techniques have been used in order to characterize the phase.

Experimental

Samples of α-PVDF films with thickness of $\sim 30\mu$ m were obtained by spreading a solution of PVDF (Solef 1100 from Solvay)) in N,N-Dimethylformamide (DMF) on a glass slide. The initial concentration of the solution was 20% of PVDF. The system was kept inside an oven at a controlled temperature of $120^{\circ}C$ for 60 min . This time was sufficient to ensure the removal of the solvent by evaporation and the isothermal crystallization of PVDF. After solvent evaporation, the sample was melted at $220^{\circ}C$ for 10 minutes, removed from the oven and cooled down at room temperature. The polymer obtained by this procedure is predominantly $\alpha -$ PVDF.

Isothermal crystallization from the melt was studied using a hot stage Linkam TMS-92 furnace operating in a N_2 atmosphere. The following procedure was employed for all samples: the samples were kept for 10 min at $220^{\circ}C$ to destroy their thermal history and remove any residual crystallinity and then quenched ($30^{\circ}Cmin^{-1}$) to their crystallization temperature T_c(150,155,160 and $165^{\circ}C$). Images of spherulite growth during the crystallization of PVDF were obtained by an optical microscope with polarized light (Olympus BH-2) and images were taken using a Leica DFC-280 camera.

Differential scanning calorometry experiments was performed with a Mettler Toledo DSC 821^e using 40μ L aluminium cans. Polymer samples were heated from 25 to $200^{\circ}C$, at a constant heating rate of $10^{\circ}Cmin^{-1}$ using high purity argon as a purge gas. The crystalline

phase (or phases) present in each sample was confirmed by infrared (Spectrum 100 Perkin-Elmer apparatus) and Raman (Jobin-Yvon *T*64000 triple-grating spectrometer + CCD detector. Excitation 514.5 nm , from Ar laser in backscattering.) apparatus.

Results and Discussion

Fig. 1 shows snapshots of the evolution of the the microstructure obtained for the samples crystallizing at 165°C. Samples crystallized at lowest temperatures (150°C and 155°C) have only one type of spherulites, corresponding to the α-phase of the PVDF [7]. The material crystallized at 150°C has the finest microstructure among the samples prepared in this work. With increasing crystallization temperature, the diameter of the spherulites also increases.

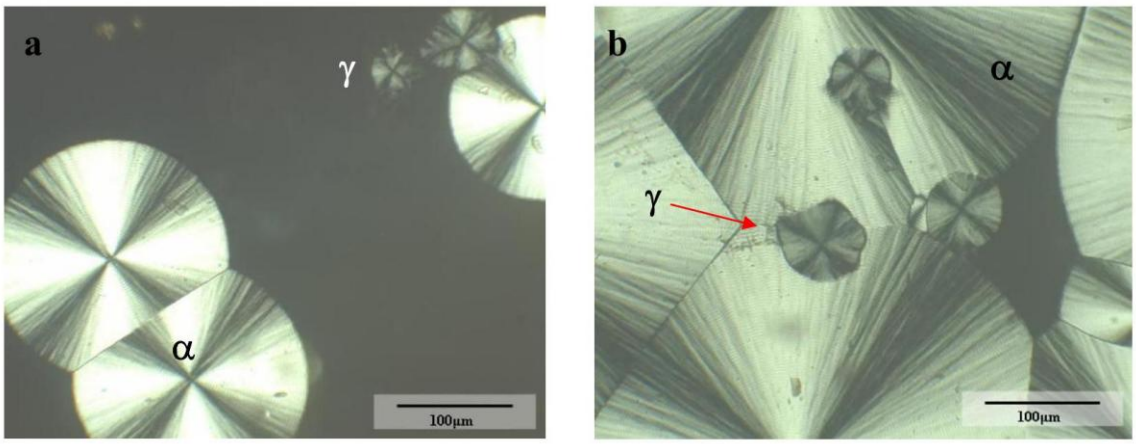

Fig. 1. Crystallization of PVDF at 165°C. Both $\gamma-$ and $\alpha-$ phase spherulites can be observed.

For crystallization temperatures higher than 160°C, a new type of spherulites emerges in the material. These spherulites are smaller and darker than the others (see fig. 1, for crystallization at 165°C) and represent the crystallization of PVDF in the γ-phase. The spherulites in the γ-phase are much smaller and enter inside of the α-phase spherulites, leaving behind it a comet-like tail that deforms the polymer matrix.

Figure 2 shows the variation of the radius of the γ-spherulites with time. For the lowest temperatures the polymer crystallizes faster giving rise to smallest spherulites.

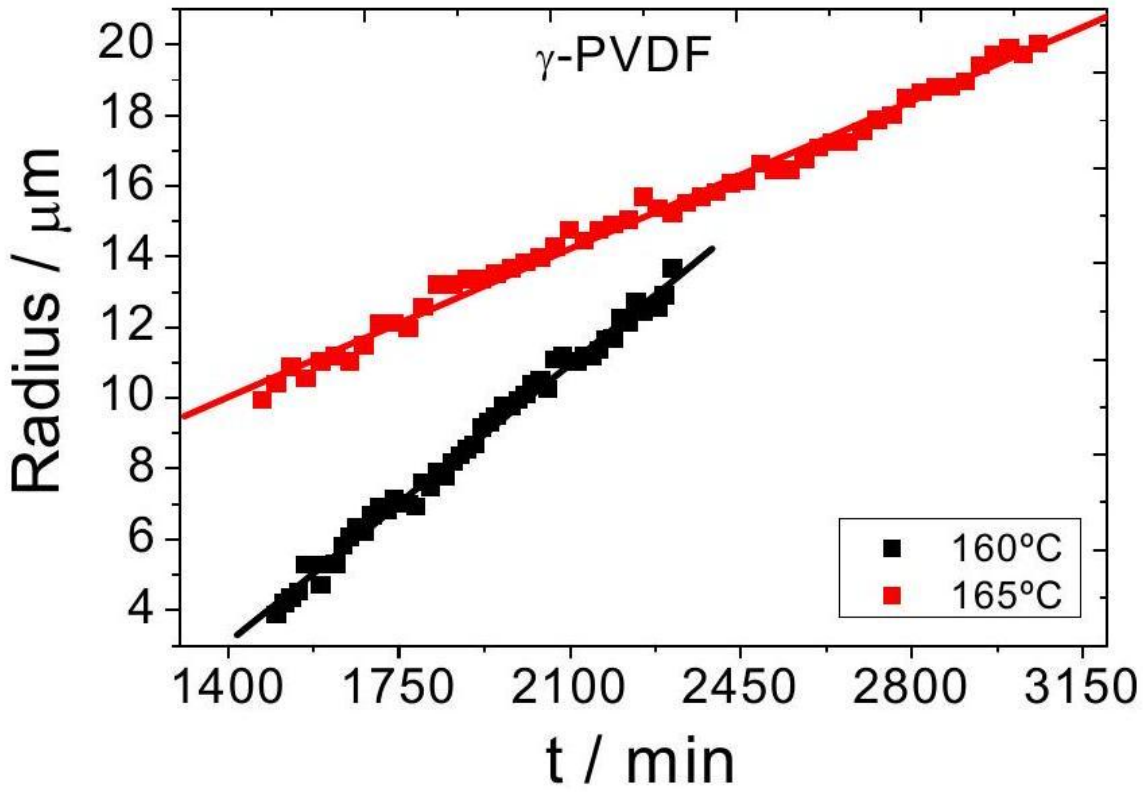

Fig. 2. PVDF spherulitic growth for different crystallisation temperatures. The crystallization rate decreases with increasing crystallisation temperature. For each crystalisation temperature, the spherulite radius, R, increases linearly with time, indicating a constant growth rate throughout the crystallization process.

The degree of crystallinity of the samples slightly decreases for increasing temperatures, as can be deduced from the area of the melting peak of the DSC curves (fig. 3). For temperature below 160 °C one single melting peak is observed, related to the α-phase of PVDF. For crystallization temperatures of 160°C and higher, two melting peaks above the melting temperature of the α-phase material are observed. The two peaks correspond to the two types of γ-phase material present in the samples: γ-phase obtained from transformation of α-phase material and γ-phase directly crystallized from the melt.

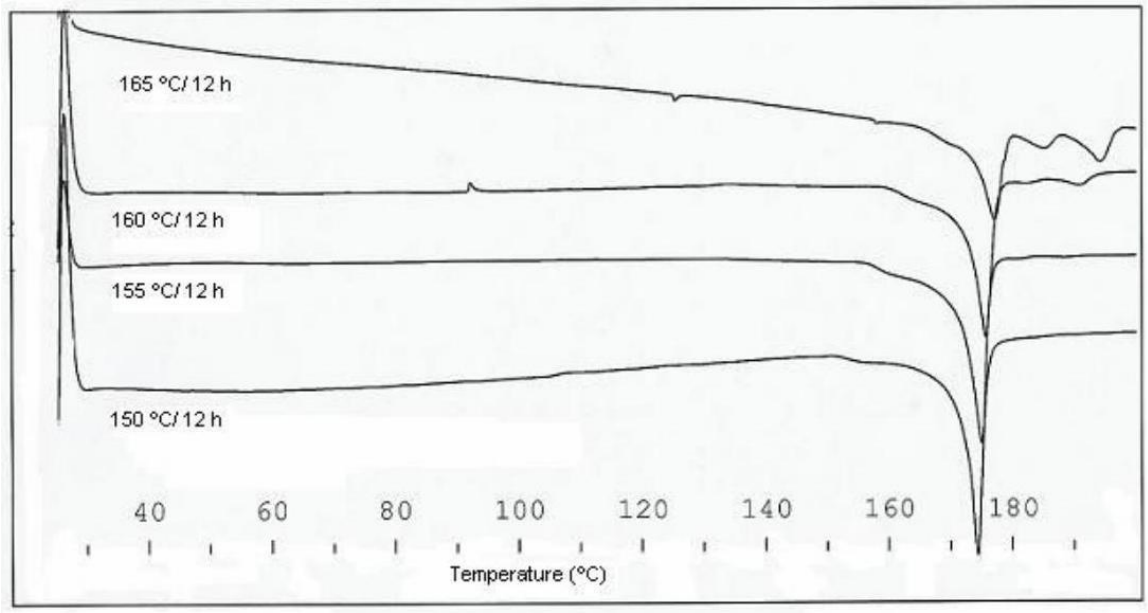

Fig. 3. DSC thermograms for the different samples.

The appearance of the γ polymorph is also detected in the far infrared and Raman spectra (fig. 4). The infrared spectra for samples crystallized at different temperatures for 12 hours confirmed that the material obtained for crystallization at lower temperatures is exclusively in the α-phase. The presence of the γ-phase is only detected for the samples crystallized at temperatures of 160°C and higher (fig. 4, left). The amount of γ-phase also depends on the crystallization time (fig. 4, right). As observed on fig. 4, left, increasing crystallization time at 165°C induce the emerging of the γ-phase, as indicated by the corresponding mode at 810 cm^{-1}. The γ-phase at this temperature appears directly by crystallization from the melt and not by phase transformation from the α-phase.

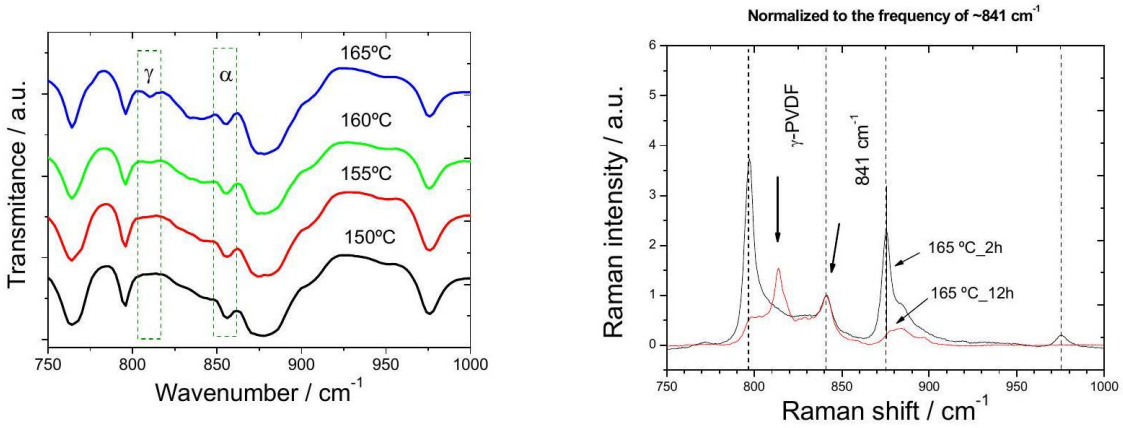

Fig. 4. FTIR results for PVDF samples crystallised at different temperatures (left) and Raman spectra for samples crystallised at 165°C for 2 and 12 hours (right).

Increasing crystallization time at 165°C induce the emerging of the γ-phase, as can be observed in the corresponding mode at 810 cm^{-1} (left). This phase at this temperature appears from crystallization of PVDF in the γ-phase.

Conclusions

Poly(vinylidene fluoride) has been obtained by isothermal crystallization from the melt at different crystallisation temperatures and the growth kinetics has been obtained. For lower temperatures, the rapid growth of the spherulites results on smaller spherulites in the final crystallised samples. For temperatures below 160°C the samples contain exclusively PVDF in the α-phase. For higher temperatures γ-phase spherulites also crystallise in the samples. The γ-phase spherulites are of two types: those directly crystallised from the melt and those transformed from the a-phase material. The two types of spherulites show different thermal stability.

Acknowledgments

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