

# Molecular Dynamics of Poly(glycolide-co-L-Lactide) Copolymer During Isothermal Cold Crystallization

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**ABSTRACT:** Poly(glycolide-co-L-lactide) (PGA/PLLA) is a random copolymer with 92 wt % PGA, being the basic resin for Vicryl<sup>®</sup> suture. Molecular dynamics of PGA/PLLA in its wholly amorphous state and during isothermal cold crystallization at 70 and 80°C have been analyzed. Experimental results were generated over a wide range of frequency and temperature by broad-band dielectric spectroscopy (DRS). The variation of the average relaxation time (defined as  $\tau = [1/2]\pi f_{\max}$  where  $f_{\max}$  is the frequency at maximum loss for the main  $\alpha$  relaxation) has been studied during cold crystallization and the temperature dependence of this average relaxation time for wholly amorphous and crystallized samples has been analyzed. This behavior has been modeled by Havriliak–Negami, Vogel–Fulcher–Tammann, and Kohlrausch–Williams–Watts equations. The evolution profile of the dynamics (frequency at which the maximum loss appears,  $f_{\max}$ ) depends

on the crystallization temperature, being different at 80°C relatively to 70°C, which could reflect different progress of the spherulitic morphology, as it is shown by the evolution of the morphologies obtained during the crystallization processes, followed by optical microscopy. While the loss maximum (and consequently relaxation times) remains almost unmodified during the crystallization process at 70°C, for the process at 80°C the maximum first moves slightly to higher frequencies (shortening of relaxation times) and at the final stages of crystallization it moves to lower frequencies (increasing the relaxation times). Supporting evidence about the thermal behavior of the polymers has been obtained with DSC. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 584–589, 2007

**Key words:** biopolymers; dielectric relaxation spectroscopy; crystallization; molecular dynamics

## INTRODUCTION

Biodegradable aliphatic polyesters like PLLA, PGA, and their copolymers are well-known bioabsorbable and biocompatible crystalline polymers. Originally limited to commercial suture applications, they have extended their use to different areas of surgery including dental repair, fracture repair, and ligament reconstruction,<sup>1–6</sup> because of their capability of biodegradation through hydrolysis of the ester linkage and the formation of decomposition products which are normal intermediates of cell metabolism.<sup>7</sup>

On the other hand, the effect that the crystalline phase exerts on the  $\alpha$  dynamics in the amorphous phase during crystallization of polymers is an interesting and fundamental research goal. The work presented herein addresses this problem experimentally

by using broadband dielectric relaxation spectroscopy (DRS) over a wide range of frequency and temperature to monitor dynamics during cold crystallization of earlier mentioned bioabsorbable and biocompatible crystalline polymers. The use of dielectric spectroscopy to follow polymer crystallization process was first reported long ago<sup>8</sup> and used with modern techniques over the last years by several authors.<sup>9,10</sup>

As a start it is useful to ask how the segmental  $\alpha$  process in a wholly amorphous but crystallizable polymer is altered once the crystals begin to form. This has been studied experimentally by directly comparing the dielectric spectra of crystalline and wholly amorphous samples and by continuously monitoring the dielectric response during crystallization. The effect of crystallinity on the average relaxation time  $\tau$  (related to the frequency of the maximum loss) for the  $\alpha$  process has been found to be complex and dependant of the type of polymer.<sup>11,12</sup> How one can account for these different trends in  $\tau$  is of fundamental interest.

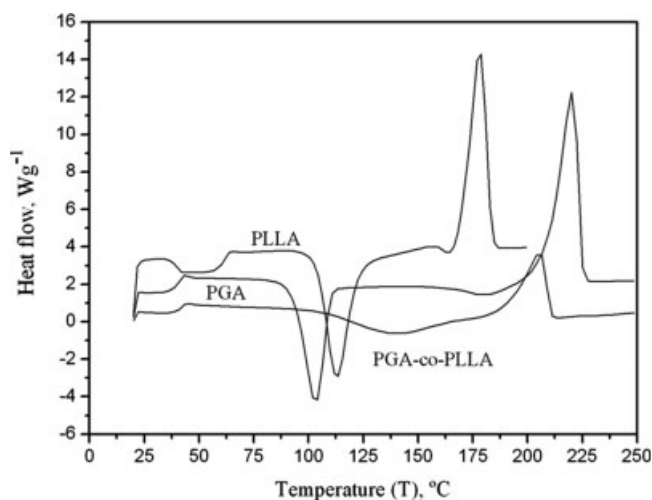
The principal objectives of this preliminary study are (1) to investigate the effect of cold crystallization on molecular (dipole) dynamics in PGA/PLLA by DRS over a wide range of frequency and temperature and

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**Figure 1** DSC thermogram of wholly amorphous PLLA, PGA, and PGA/PLLA.

(2) to elucidate the effect that the crystalline phase exerts on the  $\alpha$  process before and during cold crystallization comparing the dielectric response of amorphous and crystallizing samples. The behavior is modeled by the Havriliak–Negami and Vogel–Fulcher–Tammann equations and the corresponding parameters are obtained.

## EXPERIMENTAL

The biopolymer studied in this work, poly(glycolide-co-L-lactide) (PGA/PLLA), was kindly supplied by Ethicon Johnson and Johnson with a  $M_w$  of about 80,000 g/mol. PGA/PLLA is a random copolymer with 92 wt % PGA being the basic resin for Vicryl\* suture.<sup>13</sup> DRS measurements were carried out in a Novocontrol Alpha high-resolution dielectric analyzer that covers a frequency range between 3  $\mu$ Hz and 10 MHz. The instrument is interfaced to a computer and equipped with a Novocontrol Novocool cryogenic system for the temperature control. Further details regarding the acquisition and evaluation of data are available elsewhere.<sup>14,15</sup> Supporting evidence was obtained from differential scanning calorimetry (DSC) by using a Mettler Toledo DSC822 with scans at 10°C/min and Optical Microscopy (Nikon Eclipse E600 equipped with Mettler FP82 HT hot stage device).

## RESULTS AND DISCUSSION

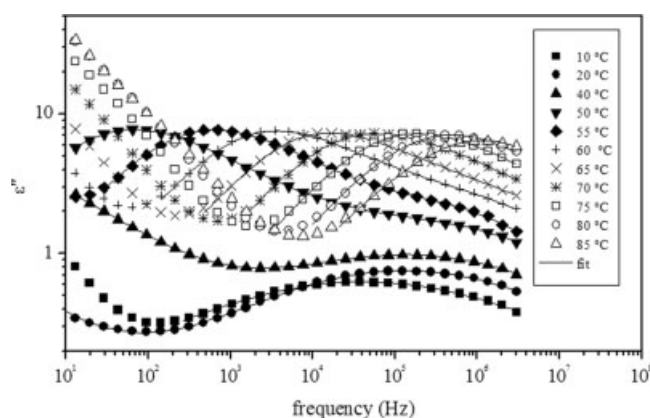
Two approaches are undertaken to investigate the effect of crystallization on the molecular dynamics of the copolymer. The first approach consists on analyzing the relaxation spectra of wholly amorphous sample. The second one focuses on *in situ* monitoring of the dielectric response during isothermal cold crystallization. For melt crystallization the frequency

window used is not enough to follow the evolution of the main relaxations (higher frequencies are needed), so in this preliminar work just the effect of cold crystallization is analyzed. Before presenting DRS results, we briefly review the thermal behavior of the copolymer as evaluated by DSC.

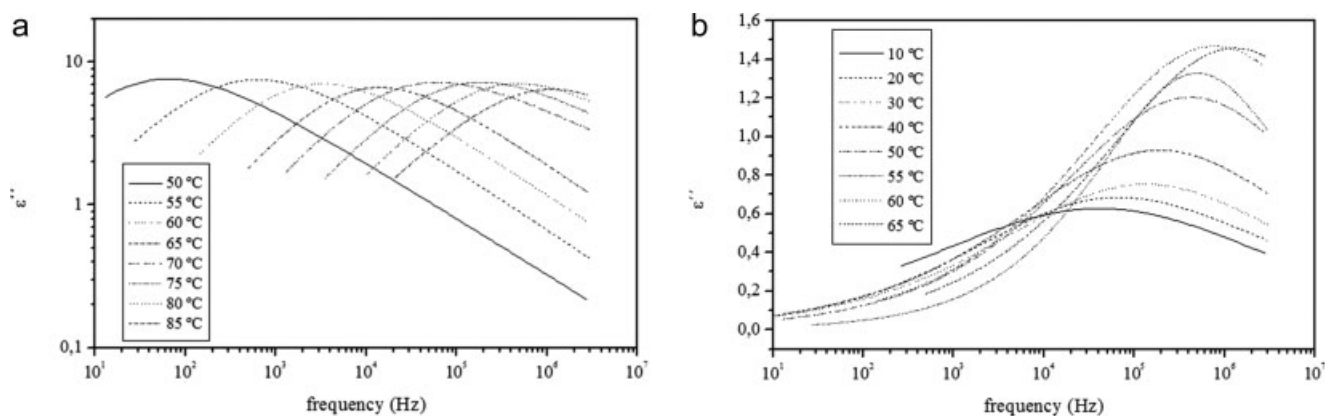
DSC thermogram for the wholly amorphous copolymer is shown in Figure 1. The thermograms of the PGA and PLLA homopolymers are also presented to compare. Traces were obtained on heating samples quenched from the melt into liquid nitrogen, rendering the sample wholly amorphous. The glass transition is observed at around 45°C for PGA/PLLA, higher than the transition of PGA homopolymer (close to 40°C). Cold crystallization and melting occur at 140 and 205°C for the copolymer and at 105 and 220°C for PGA, noting that PLLA portions (with higher glass transition and cold crystallization temperatures of 65 and 115°C respectively, and lower melt temperature of 180°C) increase the glass transition and cold crystallization temperatures and decrease melt temperature in the copolymer respecting to PGA homopolymer. Furthermore, the peak corresponding to crystallization is broader in the copolymer than in the homopolymer, thus indicating a longer crystallization, as it is shown below. All values obtained are in agreement with those found in literature.<sup>13</sup>

Concerning dielectric results, the relaxation behavior of the wholly amorphous sample is examined first. Since the permittivity and loss are related by Kramers–Kronig transform, only loss data are presented in the figures. Figure 2 shows the dielectric loss in the frequency domain with temperature as a parameter for wholly amorphous PGA/PLLA. Solid lines represent the modeling by Havriliak–Negami equation.

A low intensity  $\beta$  relaxation is observed below  $T_g$ , as it can be seen in data between 10 and 40°C. The  $\alpha$



**Figure 2** Dielectric loss in the frequency domain with temperature as a parameter for wholly amorphous PGA/PLLA. Solid line indicates Havriliak–Negami equation.



**Figure 3** Isolated (a)  $\alpha$  and (b)  $\beta$  relaxations as obtained by deconvolution from Havriliak–Negami model.

process is clearly seen at temperatures higher than  $T_g$ . Below these temperatures this process overlaps with conductivity (as high loss values indicate) and a physically meaningful deconvolution is not feasible. The  $\alpha$  process is thermodielectrically complex, and the loss peak becomes slightly narrower with increasing temperature. This behavior has been modeled by Havriliak–Negami equation, isolating both relaxations and conductivity term and obtaining relaxation time ( $\tau$ ) values, for being compared with those obtained for crystallizing samples. The Havriliak–Negami formalism proposes an analytical expression for the complex dielectric permittivity as

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (i\omega\tau_0)^b]^c} \quad (1)$$

where  $\varepsilon_0 - \varepsilon_\infty = \Delta\varepsilon$  is the dielectric strength,  $\tau_0$  is the central relaxation time, and  $b$  and  $c$  are parameters, which describe the shape of the relaxation time distribution function (symmetric and asymmetric broadening).<sup>16</sup> To describe the whole spectrum, the Havriliak–Negami equation must be combined with the following conductivity term:

$$\varepsilon_c'' = \left( \frac{\sigma}{\varepsilon_0\omega} \right) \quad (2)$$

where  $\varepsilon_0$  denotes the vacuum permittivity and  $\varepsilon_c''$  is the conductive contribution of the loss factor.

Dielectric loss data of the  $\alpha$  process have been also fitted to the Kohlrausch–Williams–Watts (KWW) or stretched exponential expression:<sup>17</sup>

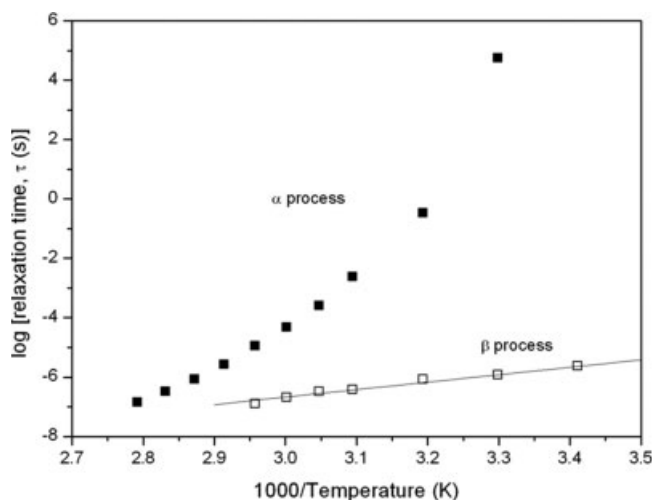
$$\Phi(t) = \exp[-(t/T)^\beta] \quad (3)$$

where  $\Phi(t)$  is the normalized relaxation function,  $\tau$  is the characteristic relaxation time and  $\beta$  is the stretched exponential parameter ( $0 < \beta < 1$ ). The exponential parameter varies very slightly with temperature. As an example, a value of 0.41 is obtained

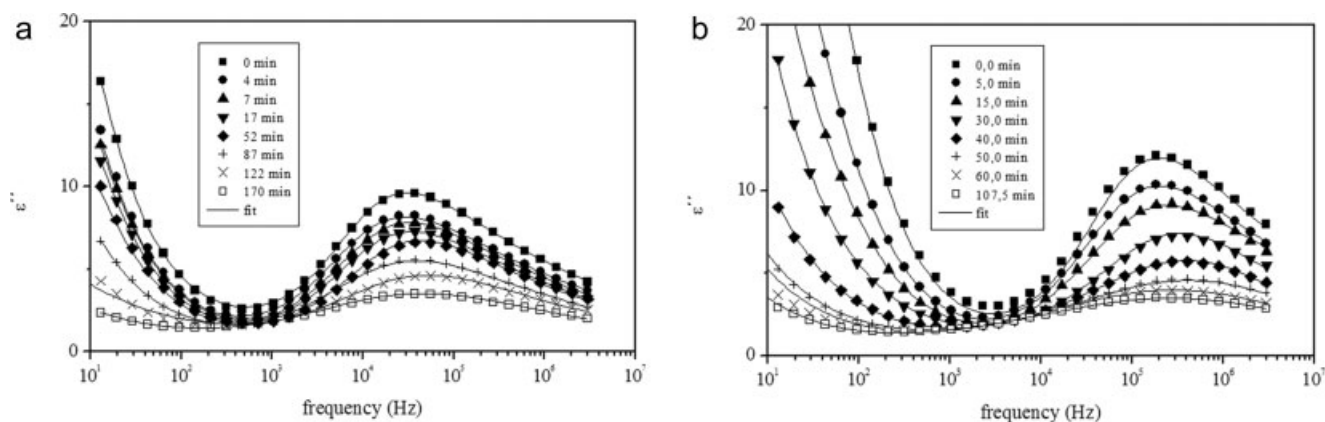
at 50°C while at 85°C the value is of 0.49. These values are in agreement with those obtained by Mijovic et al. for similar polymers.<sup>14</sup>

Figure 3(a,b) show the isolated  $\alpha$  and  $\beta$  processes respectively, obtained from the Havriliak–Negami modelization after subtracting the conductivity term. It can be seen that the  $\beta$  process is not present only at temperatures below  $T_g$ , but overlaps with the main relaxation at higher temperatures. Relaxation times are obtained from the isolated  $\alpha$  and  $\beta$  processes.

The temperature dependence of these relaxation times is examined next. In Figure 4 relaxation times obtained from Havriliak–Negami are plotted as a function of reciprocal temperature for wholly amorphous PGA/PLLA. It is well known that the  $\alpha$  process in glass-formers deviates from a thermally activated Arrhenius functional form and that a stronger temperature dependence is observed. Such behavior is generally modeled by the Vogel–Fulcher–Tammann equation, represented by the solid line in Figure 4.



**Figure 4** Relaxation time as a function of reciprocal temperature for wholly amorphous PGA/PLLA. Solid line indicates fitting to Vogel–Fulcher equation.

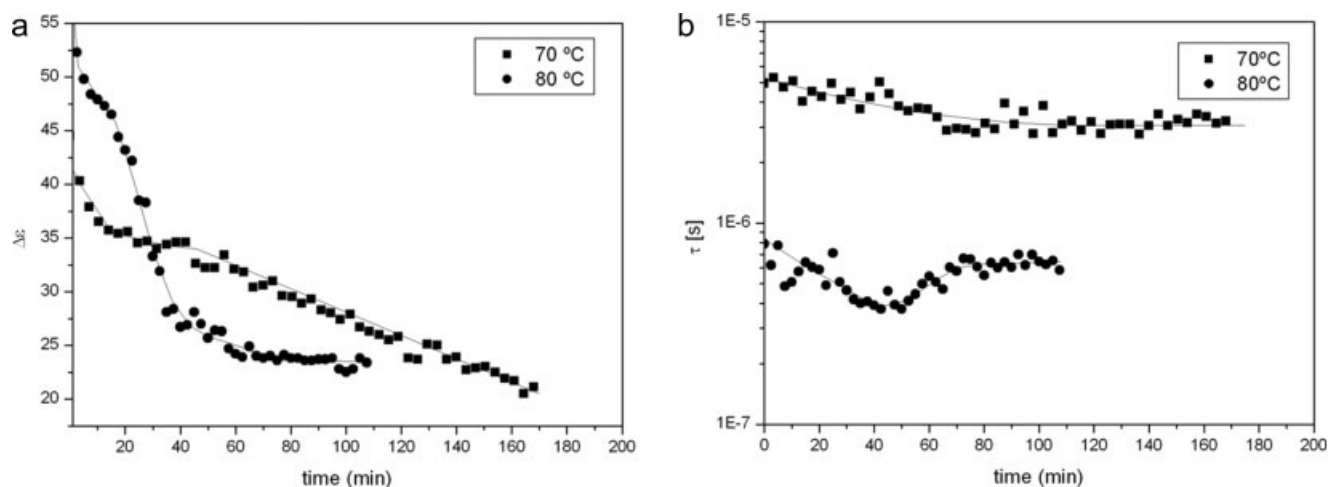


**Figure 5** Dielectric loss in the frequency domain with time as a parameter during the cold crystallization process of PGA/PLLA at (a) 70°C and (b) 80°C.

The fit parameters are  $\tau_0$  (attempt frequency) =  $2.5 \text{ E}^{-15} \text{ s}^{-1}$ ,  $B = 1516 \text{ K}$ , and  $T_v$  (Vogel temperature) =  $260 \text{ K}$ . The mean square deviation of the fitting is of  $0.04$ . All these values fall in the same range than those found in the literature for the PGA<sup>18</sup> and PLLA homopolymers.<sup>14</sup> The relaxation time of the  $\beta$  process has an Arrhenius temperature dependence, represented by the solid line in Figure 4, with the following fitting parameters:  $\tau_{\beta\infty}$  (that corresponds to a molecular vibration time) =  $6.79 \times 10^{-7} \text{ s}$  and  $B$  (a magnitude identifiable with a real energy barrier) =  $2509.63 \text{ K}$ . The mean square deviation of the fitting is of  $0.079$ . As a conclusion, the experimental facts clearly indicate that the  $\beta$  relaxation arises from molecular mobility which remains even in the glassy state (below  $T_g$ ). The molecular motion must be quite different from the main relaxation, where the relaxation time varies rapidly with temperature according Vogel–Fulcher–Tammann equation, in stark contrast with the much milder Arrhenius dependence of the relaxation time of the  $\beta$  process.

Since the molecular origin of a relaxation process is generally related to its morphological environment, it was anticipated that much could be learned about relaxation dynamics by monitoring dielectric response during the temporal evolution of crystalline morphology.<sup>14</sup> This goal was accomplished by conducting *in situ* real-time DRS measurements during cold crystallization of samples. We emphasize that the spectra recorded in each sweep are representative of an isostructure (constant degree of crystallinity) at a given stage of crystallization, because the time scale for a sweep is short (less than  $40 \text{ s}$ ) in comparison with the time scale for crystallization. Isothermal frequency sweeps were carried out for PGA/PLLA (after melting and quenching) at  $70$  and  $80^\circ\text{C}$  with time as a parameter. Figure 5(a,b) show dielectric loss in the frequency domain at different times during crystallization of PGA/PLLA at  $70$  and  $80^\circ\text{C}$ , respectively. Solid lines indicate the modeling by Havriliak–

Negami equation. The spectrum was deconvoluted as sum of a conductive contribute and the structural relaxation process, as has been shown earlier. Figure 6(a,b) show the evolution of the  $\Delta\epsilon$  and  $\tau$  fitting parameters respectively, during the crystallization process of PGA/PLLA at  $70$  and  $80^\circ\text{C}$ . The crystallization process is faster at  $80$  than at  $70^\circ\text{C}$ . The magnitude of the loss peak and the relaxation strength decrease for both crystallization temperatures. In a first approximation, the dielectric strength of a relaxation process is proportional to the total amount of relaxing units participating in the process. As the amount of relaxing material is continuously reduced by crystal formation due to the progressive transfer of a fraction of the amorphous material to the growing crystalline phase, the dielectric strength is clearly reduced. The decreasing is more pronounced for the crystallization process at  $80^\circ\text{C}$ , as can be seen in Figure 6(a), due to the faster crystallization process than at  $70^\circ\text{C}$ . The effect of crystallinity on the average relaxation time  $\tau$  (related to the frequency of the maximum loss) for the  $\alpha$  process has been found to be complex and dependant on the type of polymer and crystallizing temperature.<sup>14,19–21</sup> For the crystallization process at  $70^\circ\text{C}$ , the maximum loss of the copolymer (and consequently relaxation times) remains almost unchanged. Moreover, relaxation times obtained from these spectra are very close to those obtained for the wholly amorphous copolymer at  $70^\circ\text{C}$  ( $\tau = 4.2 \times 10^{-6} \text{ s}$  for amorphous sample in Fig. 2 and  $\tau = 4.9 \times 10^{-6} \text{ s}$  for  $t = 0 \text{ min}$  in Fig. 5), thus indicating that the initiation and development of crystallization process does not affect the relaxation time. The evolution of the relaxation time with crystallization time in Figure 6(b) supports this fact showing the low change of its value during the crystallization process. Many authors have found the same trends working with flexible-chain homopolymers like PVDF, homopolymer blends like PVDF/PMMA and blends containing block copolymers (PBT/PC).<sup>22–24</sup>



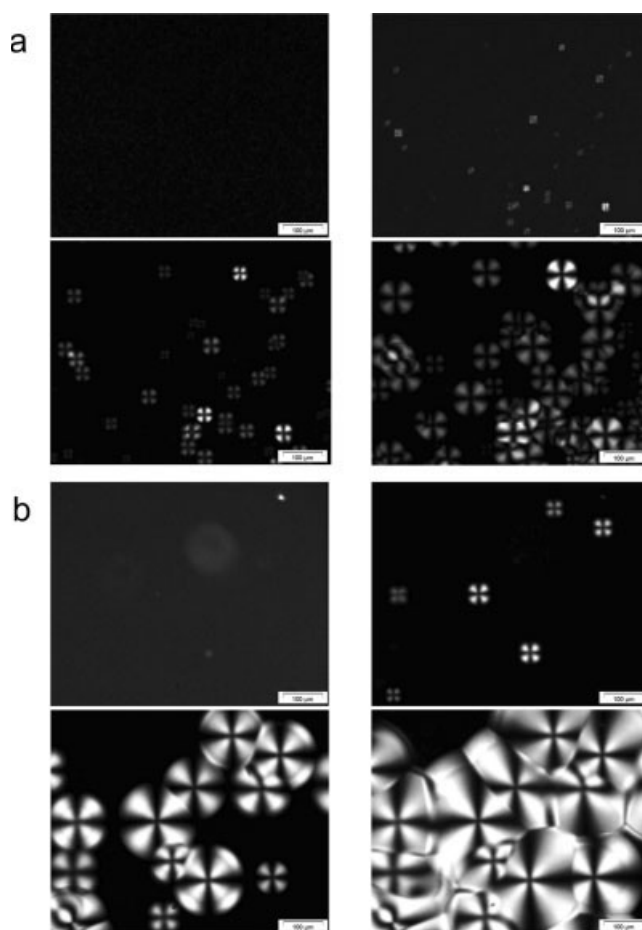
**Figure 6** Evolution of Havriliak–Negami fitting (a)  $\Delta\epsilon$  and (b)  $\tau$  during the crystallization process of PGA/PLLA at 70 and 80°C. Solid lines are guides for the eye.

For Mijovic et al.<sup>14</sup> this insensitivity of the segmental dynamics to the difference in the degree of crystallinity implies that the domain size of this segmental motion is sufficiently small that the growing crystals do not perturb dipole relaxation, what is to say that the characteristic size of the cooperatively rearranging domains is less than the thickness of the amorphous layer between lamellae. Our group proved this fact for PLLA by dielectric and atomic force microscopy study.<sup>25</sup> As it can be seen in Figure 5(b), for the crystallization process at 80°C, the loss maximum deviates first slightly to high frequencies and only at the longest crystallization times it deviates to lower frequencies as found for polyesters like poly(L-lactide) by other authors,<sup>19,20</sup> thus indicating that the development of crystalline domains affects the average segmental mobility in the amorphous phase acting as constraints and making relaxation times longer. The evolution of the relaxation time during crystallization is shown in Figure 6(b).

The evolution profile of the dynamics (frequency at which the maximum loss appears,  $f_{\max}$ ) depends on the crystallization temperature, being different at 80°C relatively to 70°C, which could reflect different progress of the spherulitic morphology.

To facilitate the visualization of the development of crystals and obtained morphologies, Figure 7(a,b) show a series of optical micrographs taken at different times during cold crystallization of PGA/PLLA at 70 and 80°C, respectively, the same conditions than in DRS. As it was shown earlier with DRS measurements, crystallization process is longer at 70°C, and also obtained spherulitic morphologies are different. At 70°C, the number of spherulites is higher (probably due to a higher nucleation rate) than at 80°C, in which there are less spherulites but larger and more perfect (probably due to a higher growing rate). This preliminary study will be com-

pleted by monitoring the crystallization process with atomic force microscopy, for a detailed analysis of the obtained morphologies.



**Figure 7** Series of optical micrographs taken during the cold crystallization process of PGA/PLLA: (a) at 70°C and 0, 30, 60, and 150 min and (b) at 80°C and 1, 15, 50, and 100 min.

## CONCLUSIONS

The following conclusions were made regarding the segmental  $\alpha$  dynamics in PGA/PLLA measured by DRS before and during crystallization. The intensity and the dielectric relaxation strength of the  $\alpha$  process decrease with increasing degree of crystallinity. The evolution of the frequency at which the loss maximum appears (related with relaxation time) depends on the crystallization temperature, which could reflect different progress of the spherulitic morphology. At 70°C, the maximum (and consequently relaxation time) remains almost unaffected by the formation of lamellar crystals, indicating that the domain size of this segmental motion is sufficiently small that the growing crystals do not perturb dipole relaxation. At 80°C, the maximum deviates first at higher frequencies and only at long crystallization times deviates to lower frequencies.

Obtained morphologies are slightly different at 70 and 80°C. Larger spherulites are formed at the higher temperature probably due to a higher growing rate, while at 70°C there seems to be a larger number of smaller spherulites probably due to a higher nucleation rate.

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