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The β relaxation as a probe to follow real-time polymer crystallization in model aliphatic polyesters

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Abstract

The dielectric spectra of two aliphatic polyesters, poly(propylene succinate) and poly(propylene adipate), are reported. For these two model aliphatic polyesters the α and β relaxations appear simultaneously and well resolved in the experimental frequency window. During isothermal crystallization, this fact allows one to use the β relaxation to characterize the crystalline structural development while the α relaxation provides information about the evolution of the amorphous phase dynamics. In this way structural development and dynamics evolution can be characterized by a single experiment during the crystallization process. Additionally, the unambiguous determination, in the amorphous polymers, of the relaxation times for the α and β relaxations further support a close relationship between local and segmental dynamics in polyesters as proposed by the coupling model.

Keywords: Polymer crystallization; Dielectric relaxation; Polyesters

1. Introduction

Upon cooling the melt polymers either crystallize, vitrify or both. A crystallizable polymer below its equilibrium melting temperature, T_m^o, is in the supercooled liquid state (SCL). An important thermodynamic characteristic of the SCL, in the temperature window defined by its glass transition temperature T_g and T_m^o, is to be unstable due to its higher free energy as compared with that of the crystal [1]. Therefore, there is a high probability that the supercooled liquid tends to reduce its free energy by means of a first order phase transition, referred to as crystallization, by which polymer segments self-assemble forming crystals [2]. At $T > T_g$ segmental mobility in polymers is revealed by the α relaxation [3,4]. Upon crystallization, the α relaxation is strongly affected by the progressive development of the crystalline phase and therefore it can be used as a probe for polymer crystallization [5,6]. Indeed, during an isothermal crystallization process both the α relaxation and the crystallinity are simultaneously followed; a precise real-time information about the interrelation between crystalline and amorphous phases can be obtained [7–10]. In this context, less attention has been paid to the secondary or β relaxation which is related to the local dynamics [4]. The β relaxation, which is observed below and above T_g, is a faster process than the α relaxation and therefore appears in a dielectric spectroscopic experiment in a higher frequency region than that characteristic of the α relaxation [4]. Quite recently it has been shown that the β relaxation may play an important role on the glass transition [11–13]. Early dielectric experiments in an aromatic polyester, poly(ethylene terephthalate) (PET), showed that the dielectric strength of the β relaxation was inversely proportional to the amount of crystalline phase [6]. Therefore by measuring simultaneously the α relaxation, related to the segmental dynamics in the amorphous phase and very sensitive to ordering processes [5–10], and the β relaxation, associated to the local dynamics and inversely proportional

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to the amount of the crystalline phase [6], polymer crystallization could be followed in a straightforward manner. However, in most of the studied cases [2,5–10] at the crystallization temperature of interest the α relaxation appears within the frequency window covered by conventional dielectric spectrometers, typically 10^{-1}–10^{6} Hz, whereas the β relaxation is located in a frequency region well above the highest frequency limit and therefore it cannot be well characterized. In this work, we report dielectric spectroscopic measurements during the isothermal crystallization of two model aliphatic polyesters, poly(propylene succinate) (PPS) and poly(propylene adipate) (PPA), in which their glass transition temperatures are such that the α and β relaxations appear simultaneously in the conventional frequency range. This fact allows one to characterize simultaneously structural development, by using the β relaxation as a signature for it, and dynamics evolution, through modifications of the α relaxation, during the crystallization process.

2. Experimental part

2.1. Synthesis of the polymers

Poly(propylene succinate) (PPS) and poly(propylene adipate) (PPA) (see schemes in Fig. 1) were synthesized according to the well-known two-stage polycondensation procedure, as reported elsewhere [14] starting from dimethyl succinate or dimethyl adipate, respectively, and 1,3-propanediol glycol, with titanium tetrabutoxide as catalyst. The number average molecular weight (M_n), determined by GPC, turned out to be 36,400 for PPS and 31,200 for PPA. At room temperature both polymers can be easily obtained in a completely amorphous state by quenching from a temperature above their T_m ($T_m^{PPS} = 44$ °C, $T_m^{PPA} = 40$ °C). The calorimetric curves of the quenched samples are indeed characterized only by a glass transition phenomenon ($T_g^{PPS} = -29$ °C, $T_g^{PPA} = -54$ °C).

2.2. Dielectric spectroscopic measurements

Dielectric spectroscopy (DS) measures the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ as a function of frequency, where ε' is the dielectric constant and ε'' is the dielectric loss. Specimens for dielectric spectroscopy were pressed between two circular metallic electrodes of 2 cm diameter at 100 °C for PPS and 50 °C for PPA. Kapton spacers with 0.07 mm thick were used to avoid the short circuit of the two metallic electrodes. In both cases, samples were then quenched at room temperature and immediately transferred to the dielectric cell. Dielectric loss measurements $\varepsilon'' = \mathrm{Im}(\varepsilon^*)$ were performed over a broad frequency window, $10^{-1} < F\ (\mathrm{Hz}) < 10^{7}$ by means of a Novocontrol system integrating a dielectric interface (ALPHA) and a temperature control by nitrogen jet (QUATRO) with a temperature error, during every single sweep in frequency, of 0.1 K. In order to follow the crystallization process each polyester was held at an appropriate crystallization temperature ($T_c = 25$ °C for PPS and $T_c = -45$ °C for PPA). After a controlled period of time the sample was rapidly cooled down at 5 °C/min to the measuring temperature to perform a frequency sweep (2 min) and immediately heated up to T_c at 5 °C/min to wait for another time period. The measuring temperatures were selected in order to visualize both the α and β relaxation processes well resolved within the frequency window. Several initial cycles were first performed in order to remove internal stresses in the sample before start counting the time.

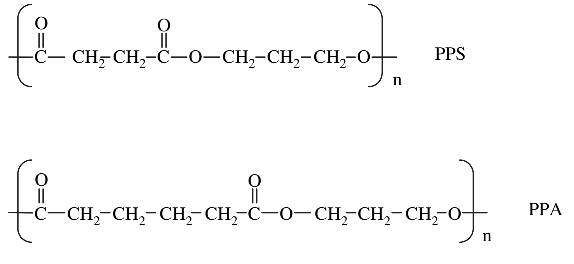

Fig. 1. Scheme of the investigated polymers: (a) poly(propylene succinate) (PPS) and poly(propylene adipate) (PPA).

2.3. Analysis of the dielectric measurements

The shape analysis of the dielectric curves was accomplished considering both α and β relaxations as being Havriliak–Negami (HN) processes [4,15]. Accordingly, dielectric loss data can be described as:

$$\varepsilon'' = \mathrm{Im}[\varepsilon^*] = \mathrm{Im}\left[\varepsilon_\infty + \sum_{x=\alpha,\beta} \Delta\varepsilon_x \left[1 + (i\omega\tau_{HN}x)^{b_x}\right]^{-c_x}\right] \qquad (1)$$

where the relaxation strength is defined as $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$, ε_0 and ε_∞ being the relaxed and unrelaxed limits of the dielectric constant [4], respectively, τ_{HN} is the central relaxation time i.e. the maximum of the relaxation time distribution function, and b and c are the shape parameters which describe, respectively, the symmetric and asymmetric broadening of the relaxation time distribution function [4]. The subscript makes reference either to the α or to the β relaxation. To estimate the accuracy of the fitting parameters, their values have been varied. We found that the maximum possible variation without provoking a significant deviation between the measured and calculated curves was less than ±5% for b, c, and $\Delta\varepsilon$, and ±10% for τ. Additionally, the frequency of maximum loss, F_{max}, can be calculated by means of the following relation:

$$\frac{1}{2\pi F_{max}} = \tau_{HN}\left[\sin\frac{b\pi}{2+2c}\right]^{-1/b}\left[\sin\frac{bc\pi}{2+2c}\right]^{1/b} \qquad (2)$$

3. Results

3.1. Dielectric relaxation of amorphous PPA and PPS

Dielectric loss, ε'' measured in the available frequency window at $T > T_g$ is shown as a function of frequency for different temperatures in Fig. 2a and b for PPA and PPS, respectively. The dielectric data show not only the α-relaxation process, at lower frequencies, but also the β-relaxation process at higher frequencies. As expected [4], the relaxations manifest themselves as maxima in ε''. As the temperature increases the frequencies of maximum loss, $F_{\max}$, shift towards higher values. At low frequencies the relaxations are accompanied by a strong increase of ε'' corresponding to a dc-conductivity contribution. Isothermal ε'' data can be phenomenologically described according to the Havriliak–Negami [4,15] (Eq. (1)). The additional contribution of the conductivity process can be taken into account by adding a term: $-i\sigma/(\varepsilon_{\mathrm{vac}}\omega^s)$ to Eq. (1). Here σ is related to the electrical conductivity, $\varepsilon_{\mathrm{vac}}$ is the dielectric constant of vacuum, and the value of the coefficient $0 < s < 1$ depends on the conduction mechanism [4,16]. The results from this phenomenological data analysis are presented in Fig. 2 by the continuous curves. For the sake of clarity, only in one case the contribution of the different processes has been illustrated. The characteristic parameters of Eq. (1) are shown in Fig. 3 as a function of temperature. It is noteworthy that no parameter extrapolation from low temperature is needed while fitting the dielectric data of Fig. 2, due to experimental accessibility to both the α and the β relaxations in the same isotherm. Dielectric strength values $\Delta\varepsilon = \varepsilon_{\mathrm{o}} - \varepsilon_{\infty}$ for the β relaxation tend to increase with temperature below T_{g}. At higher temperatures, in the merging region where the β and the α relaxations coexist, $\Delta\varepsilon_{\beta}$ values tend to decrease. The precise evolution of the dielectric strength of the β relaxation at $T > T_{\mathrm{g}}$ depends on the type of merging scenario invoked

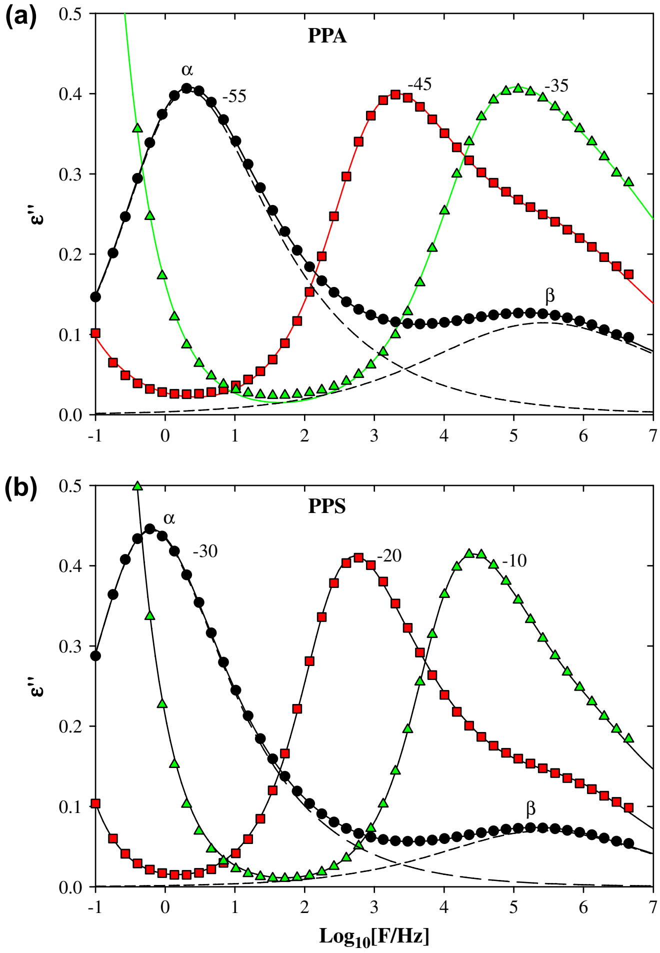

Fig. 2. Dielectric losses, ε'', of (a) amorphous PPA and (b) amorphous PPS as a function of frequency for different temperatures expressed in °C. The separation of ε'' into α and β processes have been indicated by the dashed lines for the lower temperature measurement.

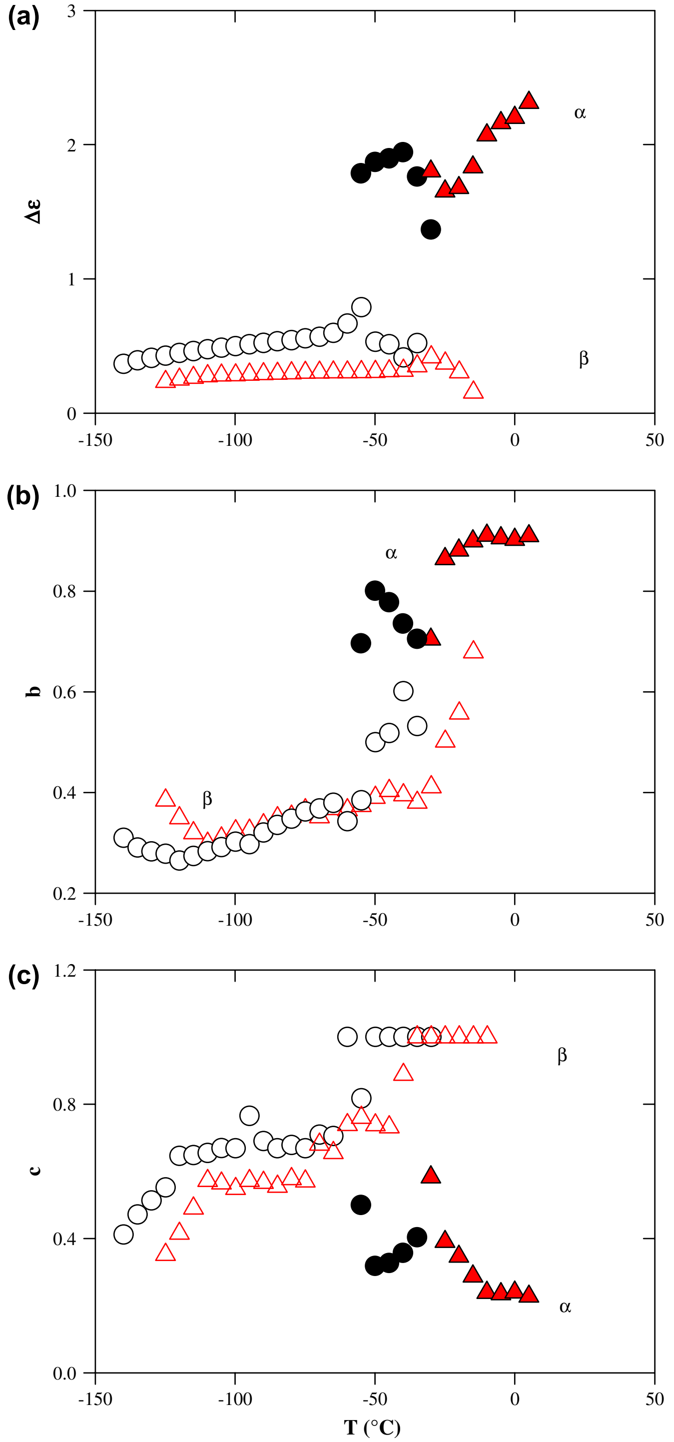

Fig. 3. Results of the fittings to the HN equation of the dielectric data of Fig. 1 for: (i) α relaxation of PPA (●) and PPS (▲) and (ii) β relaxation of PPA (○) and PPS (△). (a) Dielectric strength, (b) broadening parameter and (c) asymmetry parameter.

[4,17]. For type C, D and B the β relaxation tends to vanish overlapped by the α. This seems to be the case for PPS and PPA. Both PPA and PPS present a strongly asymmetric α relaxation as denoted by an asymmetric broadening parameter $c < 1$. On the contrary, the β relaxation is asymmetric at low temperatures but tend to become symmetric, $c = 1$, in the merging region. Qualitatively similar features have been observed in aromatic polyesters in the frequency region where the α and β relaxations merge [18]. The values of $F_{\max}$ for PPA and PPS have been represented in Fig. 4 as a function of the reciprocal temperature for both relaxations.

In such a representation, the β relaxations present clearly two regions. At lower temperatures, before the α relaxation appears, the β relaxation follows the characteristic Arrhenius behavior typical of a non-cooperative process [4,19]. The activation energy associated with this process is about 39.6 kJ/mol and 40.8 kJ/mol for PPA and PPS, respectively. These values are in the range of what is expected for polyesters [4,18,19]. However, at temperatures above the T_g of each sample, $F^{\beta}_{\max}$ values exhibit a second Arrhenius like dependence with a higher activation energy, 49.7 kJ/mol and 62.6 kJ/mol for PPA and PPS, respectively, than those found at low temperatures. In the case of the α relaxation, which appears as a consequence of the segmental motions of the amorphous phase above the glass transition temperature, the dependence of $\mathrm{Log}_{10}[F_{\max}]$ values with the reciprocal temperature exhibits a certain curvature which can be described by means of the Vogel–Fulcher–Tammann (VFT) equation:

$$\tau_{\max} = \tau_0 \exp(DT_o/(T - T_o)) \tag{3}$$

where $\tau_{\max} = (2\pi F_{\max})^{-1}$. It is noteworthy that the fits have been performed considering τ_0 as to be 10^{-14} s as recently proposed [20]. The VFT parameters in this case are, $D = 5.9$, $T_o = 181.5$ K for PPA and $D = 6.3$, $T_o = 201.6$ K for PPS.

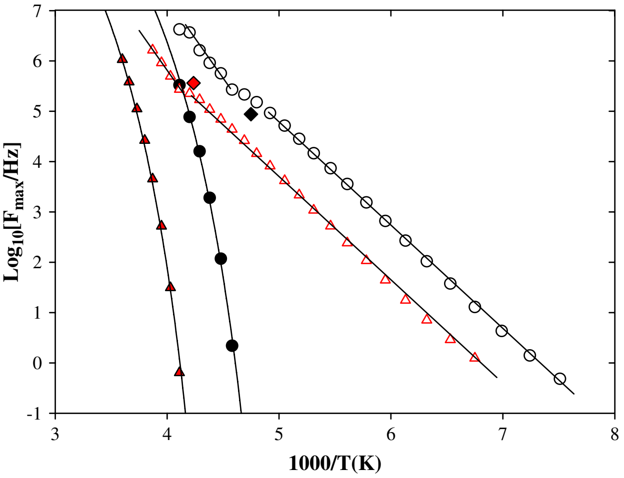

Fig. 4. $F_{\max}$ values as a function of reciprocal temperature for (i) α relaxation of PPA (●) and PPS (▲) and (ii) β relaxation of PPA (○) and PPS (△). Continuous lines for the α relaxations are the results of the fittings to the VFT equation. Continuous lines for the β relaxations are fits to Arrhenius behavior. Diamonds are the expectations according to the coupling model for (◆) PPA and (◆) PPS.

3.2. Time-resolved cold crystallization of PPA and PPS

3.2.1. Induction period

Fig. 5 shows the time-resolved ε'' data collected during the early stages of the cold crystallization experiment at $T_c = 25$ °C for PPS and $T_c = -45$ °C for PPA. At the measuring temperature of $T = -25$ °C for PPS and $T = -52.5$ °C for PPA, both relaxation processes, α and β, are well resolved and clearly visible within the frequency range. The initial amorphous state is characterized by an intense relaxation, α, associated to the segmental dynamics [4] and a less intense relaxation, β, related to the local chain dynamics [4,18,19]. In this early stage of crystallization, while the α relaxation clearly decreases in intensity with crystallization time the β relaxation remains almost unaffected. The continuous lines in Fig. 5 represent the fits of the experimental data to Eq. (1). The β relaxation can be treated as a symmetric process, $c = 1$, during the whole crystallization process. As it can be seen, during this first regime, the α relaxation suffers a significant modification while the β relaxation can be well described by the initial parameters corresponding to the initial amorphous sample.

3.2.2. Main crystallization process

Figs. 6 and 7 show, for PPS and PPA, respectively, the evolution of the dielectric relaxations with crystallization time after the initial period described above until the completion of the crystallization process. To our knowledge, no examples where the characteristics of both segmental and local dynamics

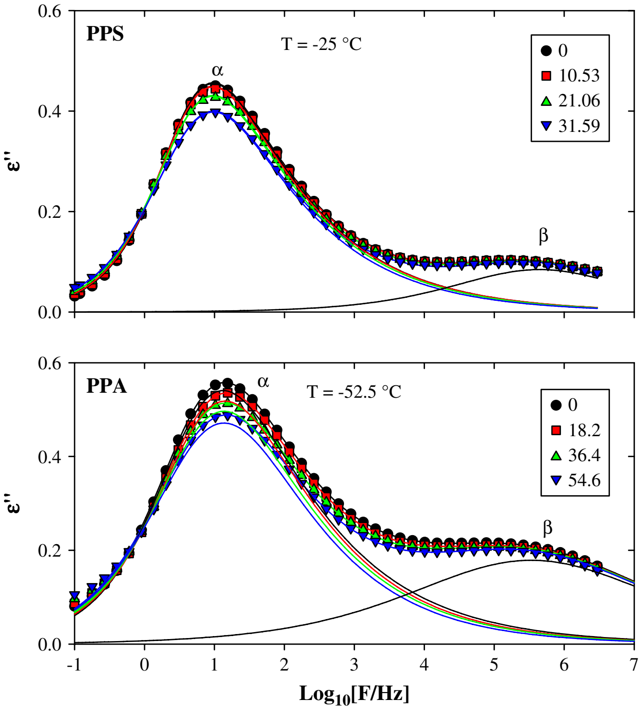

Fig. 5. Dielectric loss data in the induction period at $T = -25$ °C for PPS and $T = -52.5$ °C for PPA as a function of frequency after isothermal crystallization ($T_c = 25$ °C for PPS and $T_c = -45$ °C for PPA). The continuous lines are examples of the model Havriliak–Negami function. Legends to the symbols indicate the crystallization time.

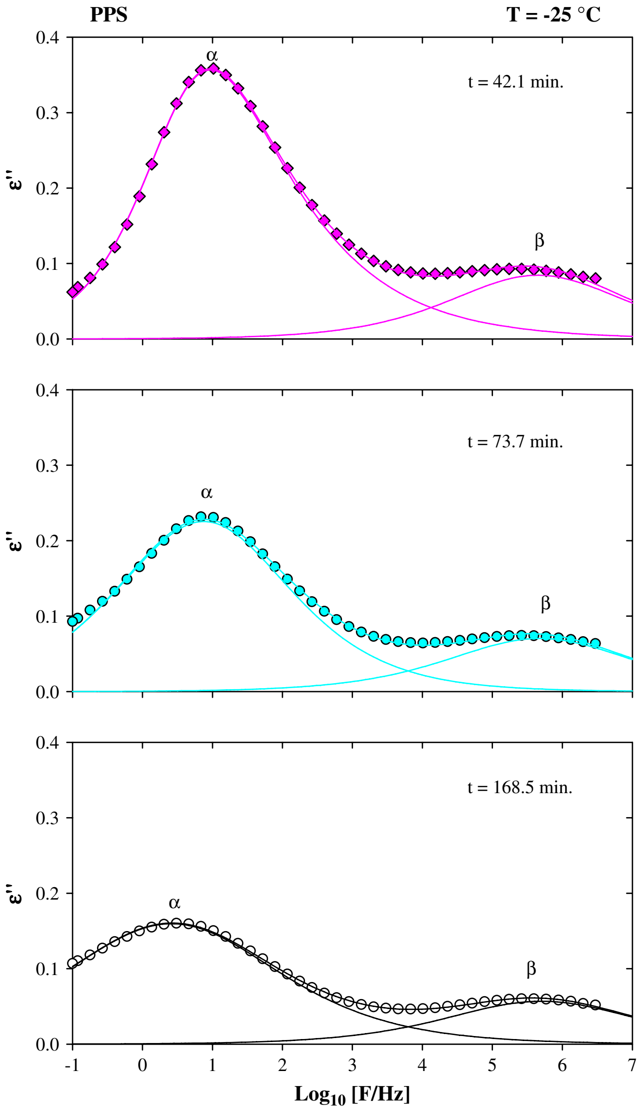

Fig. 6. Dielectric loss data at $T = -25$ °C for PPS as a function of frequency after isothermal crystallization ($T_c = 25$ °C) for different periods of crystallization time. The continuous lines are examples of the model Havriliak–Negami function.

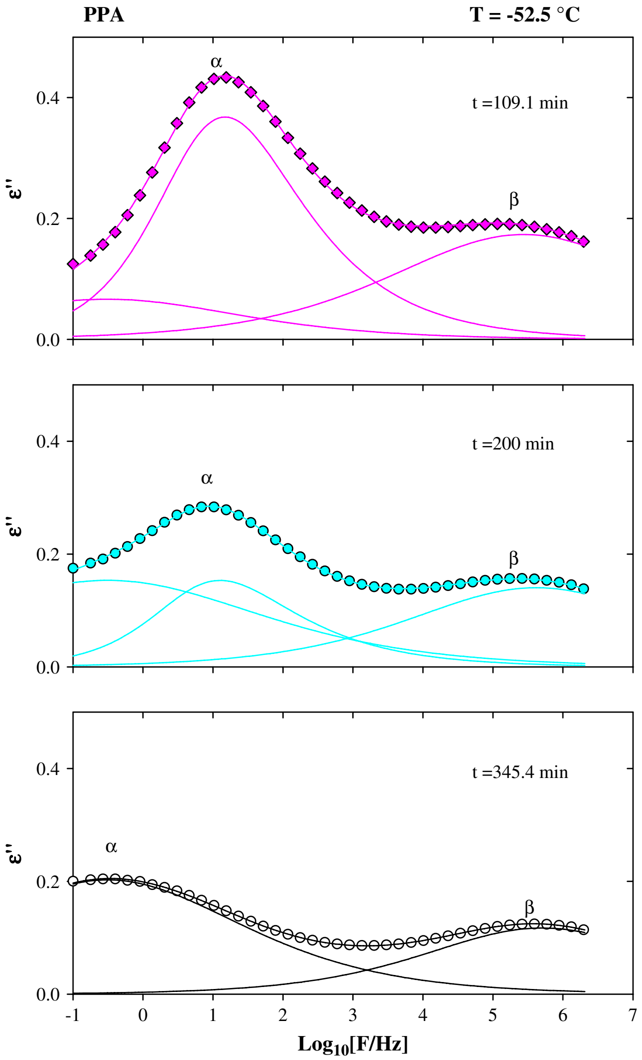

Fig. 7. Dielectric loss data at $T = -52.5$ °C for PPA as a function of frequency after isothermal crystallization ($T_c = -45$ °C) for different periods of time. The continuous lines are examples of the model Havriliak–Negami function.

are measured simultaneously during a crystallization process are reported in the literature. Here, both α and β relaxations decrease with time and, additionally, the F_{max} of the α relaxation exhibits a shift towards lower frequencies. These are characteristic signatures of a polymer crystallization process as revealed by dielectric spectroscopy [5–10]. In the case of PPS, the continuous lines in Fig. 6 represent the fits of the experimental data to the HN equation with the corresponding separation of the two relaxations. In this crystallization regime both α and β require a modification of the parameters in order to be described by the HN equation. In the case of PPA, the situation is very similar but as crystallization proceeds a significant broadening in the low frequency side of the α relaxation is detected (see Fig. 7). This effect, previously reported [8,9] for PET, can be described by an additional α-process, α', appearing at lower frequency as crystallinity develops and corresponding to the segmental relaxation of a confined amorphous phase coexisting with the initial one. Consequently an additional term in Eq. (1) must be taken into account to consider a second α-process [9]. Fig. 7 shows the separate contribution of every process as well as the total fittings where the α' relaxation at low frequency has been considered to be symmetric.

3.2.3. Evolution of the shape parameters with crystallization time

Figs. 8 and 9 show for PPS and PPA, respectively, the changes of the characteristic parameters during the crystallization process. In particular, the dielectric strength (a), the broadening parameter (b), the asymmetry parameter (c) and the F_{max} values (d) have been plotted as a function of crystallization time. Fig. 8 shows the data concerning the α and the β relaxations of PPS, while in the case of PPA, Fig. 9 presents also the data for the α' relaxation. For poly(propylene succinate), PPS, the general evolution of the shape parameters of the α relaxation follows the trend expected during a crystallization process [5–10]: (i) a reduction of the $\Delta\varepsilon_{\alpha}$ values associated to the decrease of the amorphous mobile phase which is transferred to the crystalline phase, (ii) a reduction of the b_{α} parameter indicating an increase of the broadening, (iii) an increase of c_{α} indicating a symmetrization of the relaxation and (iv) a reduction of the frequency of maximum loss, F_{max}, associated to the slowing down of the amorphous phase due to the confinement induced by the crystalline phase. The β relaxation qualitatively follows the same trend with the exception of the F_{max} values which remain essentially unchanged during the crystallization process. This is somehow expected, due to the local character of the β relaxation [4,6,19], its relaxation time is essentially not affected by the crystalline environment. For poly(propylene adipate), PPA, the trend is qualitatively similar, even though more complex due to the appearance of the α' relaxation. As crystallization proceeds the dielectric strength of the α' relaxation, $\Delta\varepsilon_{\alpha'}$, tends to increase at expenses of $\Delta\varepsilon_{\alpha}$. At the end of the crystallization process, $\Delta\varepsilon_{\alpha}$ tends to zero and the lower frequency process becomes the characteristic α relaxation of the crystallized material.

4. Discussion

4.1. Relation between the β and the α relaxation for the amorphous polymers

Due to the possibility to detect, in a single measurement, the α and the β relaxations well resolved, then the F_{max} values of the β relaxation can be unambiguously determined. In particular, Fig. 4 shows that the Arrhenius temperature dependence of the β relaxation does not persist when the α relaxation appears at temperatures above T_g. As a matter of fact, the temperature dependence of the β relaxation is complex, exhibiting an Arrhenius behavior at lower temperatures as well as to higher ones but with higher activation energy above T_g. This behavior indicates that the β relaxation is strongly affected by the glass transition and probably has a Johari–Goldstein character [11]. Although the β relaxation has been traditionally assigned to local motions, recent results show that it may play an important role on the glass transition [11–13]. Johari and Goldstein reported that β relaxations in low molecular weight rigid molecules may involve a substantial part of whole molecule. In these cases, the β relaxation is referred to as Johari–Goldstein relaxation (JG) [21]. Ngai et al. proposed that the relaxation time of the JG process at T_g, $\tau_{\beta}(T_g)$, has to be related to the primitive relaxation time, τ_o, of the coupling model (CM) which is the precursor of the α relaxation [11–13] by $\tau_{\beta}(T_g) \approx \tau_o$. According to the CM, a relation between the characteristic relaxation time of the α relaxation, τ_{α}, and the primitive relaxation exists at T_g, that is:

$$\tau_0 = (t_c)^n (\tau_{\alpha})^{1-n} \tag{4}$$

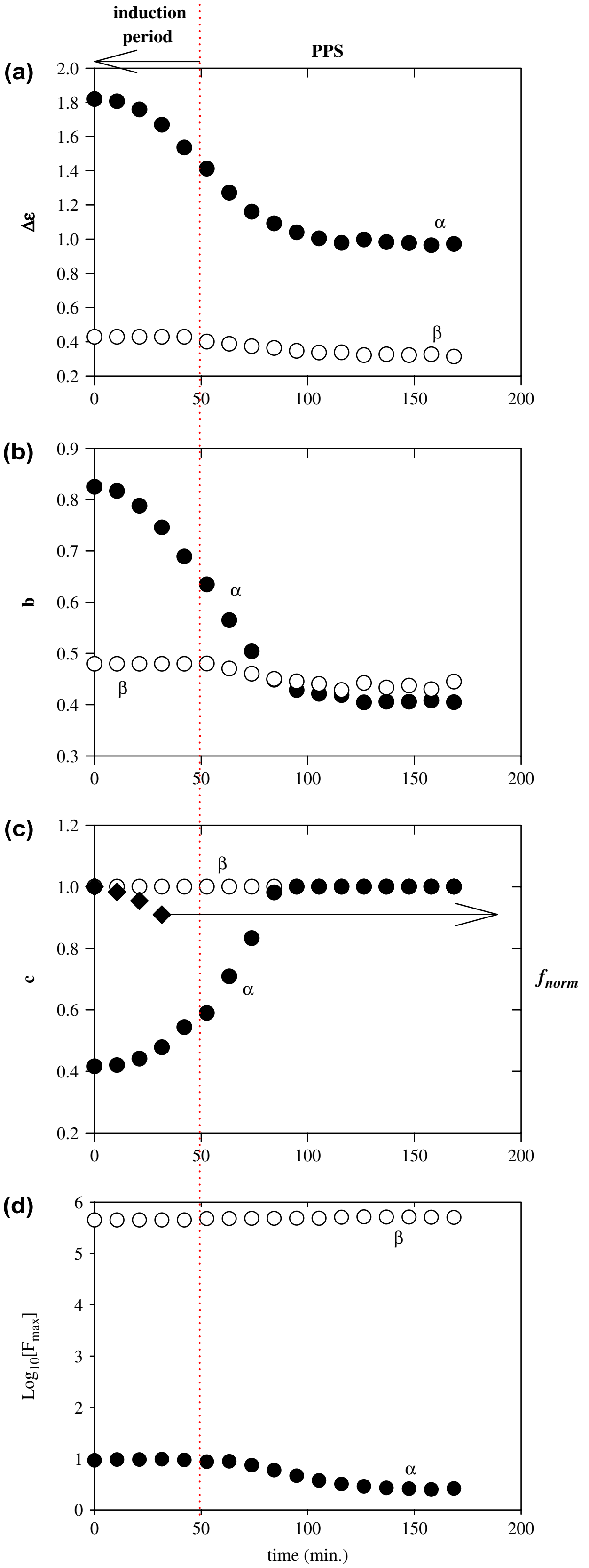

Fig. 8. Results of the fittings of the dielectric data of Figs. 5 and 6 for the α (●) and β (○) relaxations to de Havriliak–Negami equation. From the top to the bottom: (a) dielectric strength (Δε); (b) broadening parameter; (c) asymmetry parameter and (d) frequency of maximum loss. All parameters are represented as a function of crystallization time. Vertical dotted line in red indicates the limit of the induction period. Right scale on Fig. 8c corresponds to the normalized values of the reduced dielectric strength function $f(\varepsilon_0)$ (◆). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

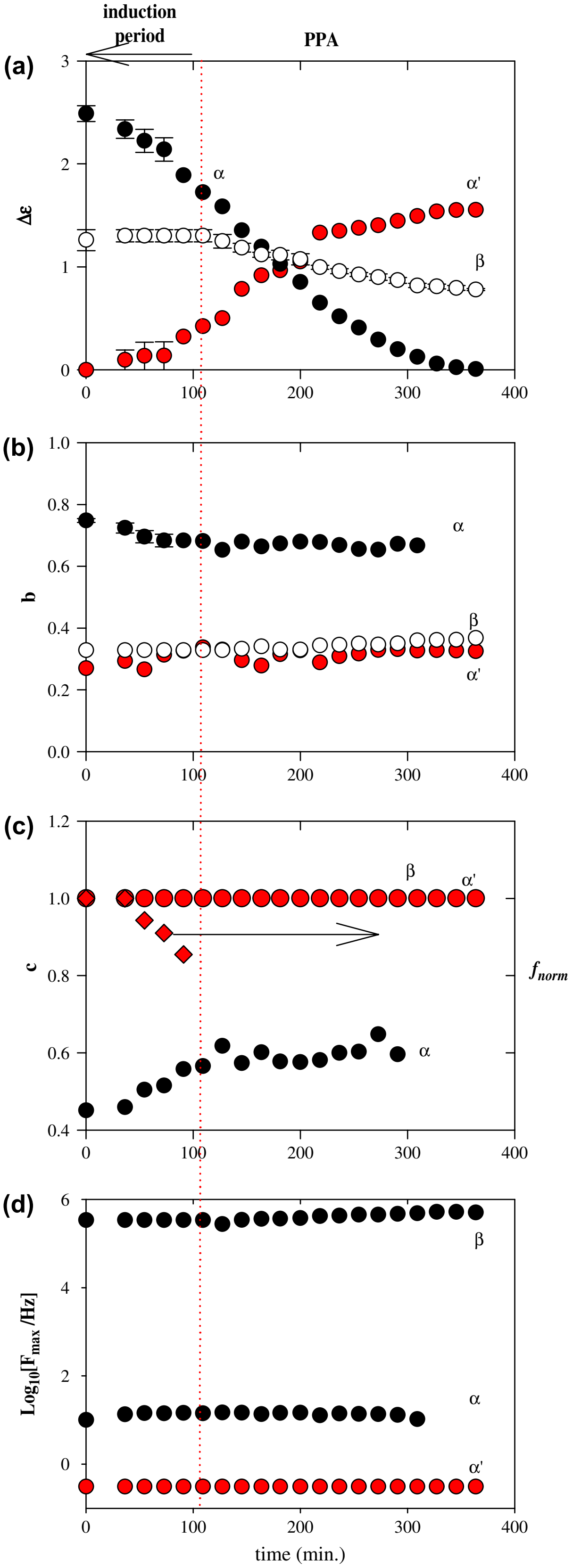

Fig. 9. Results of the fittings of the dielectric data of Figs. 5 and 7 for the α (●), α' (●), and β (○) relaxations to de Havriliak–Negami equation. From the top to the bottom: (a) dielectric strength (Δε); (b) broadening parameter; (c) asymmetry parameter and (d) frequency of maximum loss. All parameters are represented as a function of crystallization time. Vertical dotted line in red indicates the limits of the induction period. Right scale on Fig. 9c corresponds to the normalized values of the reduced dielectric strength function $f(\varepsilon_0)$ (◆). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where t_c is the crossover time from independent to cooperative relaxation, and has been estimated to be 2×10^{-12} s from neutron scattering experiments [22] and n is related to the exponent in the Kohlrausch function followed by the dipolar correlation function:

$$\phi(t) = \exp\left[-(t/\tau_\alpha)^{1-n}\right] \qquad (5)$$

Assuming that the primitive relaxation is related to the secondary process, a close relationship, governed by Eq. (4), should exist between τ_α and τ_β at T_g. This hypothesis has been shown to be valid for a great variety of glass forming systems [11–13] including aromatic polyesters [18,23]. In our case, values of the KWW exponent were calculated after Inverse Laplace Transformation of the HN functions describing the α relaxation at $T = -55$ °C for PPA and at $T = -30$ °C for PPS, respectively, and subsequently fitted to the KWW curve of the time–domain data [24]. The results provide n values of 0.57 and 0.61 for PPA and PPS, respectively. Assuming that the n values are similar at T_g and introducing these values into Eq. (4), considering $\tau_\alpha(T_g) = 100$ s as customarily accepted [25], an estimate of τ_o could be obtained. These calculations have been presented in Fig. 4 by diamonds. The calculated values of τ_o are very similar to the experimental τ_β both for PPS and PPA, providing further indication of the complex character of the β relaxation and of the close relationship between local and segmental dynamics in polyesters as proposed by the coupling model [25].

4.2. The β relaxation as a probe to follow real-time polymer crystallization

4.2.1. Main crystallization process

The main novel aspect of these measurements is that the α relaxation, related to the segmental dynamics [4] and very sensitive to ordering processes [5–10], appears in the measured frequency range simultaneously with the β relaxation associated to the local dynamics. Assuming that the dielectric strength of the β relaxation is inversely proportional to the amount of the crystalline phase [6] then a characterization of structural development and dynamics could be possible by a single experiment. In this case the magnitude defined as $X_c^{\text{diel}} = 1 - \Delta\varepsilon_\beta/\Delta\varepsilon_\beta^{o}$, $\Delta\varepsilon_\beta^{o}$ being the initial dielectric strength of the β relaxation, can be considered as an estimate of the crystallinity. Fig. 10a represents for PPS the dependence of $\Delta\varepsilon_\alpha$ as a function of X_c^{diel}. According to the Kirkwood–Fröhlich equation, the dielectric strength Δε, in a first approach, is proportional to the amount of dipoles involved in the relaxation process [26]. The data reported in Fig. 10a clearly indicate three different regimes: firstly, a period in which a strong reduction of $\Delta\varepsilon_\alpha$ occurs without a significant change in X_c^{diel};

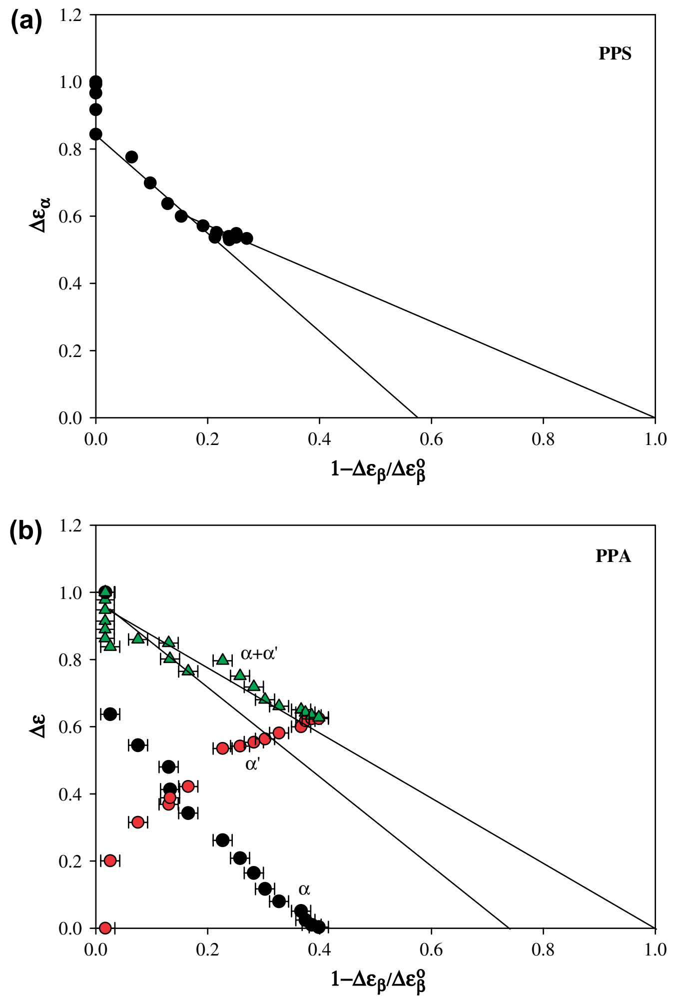

Fig. 10. Normalized dielectric strength Δε as a function of the $X_c^{\mathrm{diel}} = 1 - \Delta\varepsilon_\beta/\Delta\varepsilon_\beta^{\mathrm{o}}$ for (a) PPS and (b) PPA. The straight lines are a guide for the eye.

secondly, a region in which the reduction of $\Delta\varepsilon_\alpha$ is accompanied by an increase of X_c^{diel} according to a proportionality constant different from -1; finally a third period in which the reduction of $\Delta\varepsilon_\alpha$ becomes inversely proportional to X_c^{diel} according to a proportionality constant ≈ -1. Focusing the attention on the second and third periods, one can observe a qualitatively similar behavior with respect to the aromatic polyester poly(-butylene isophthalate) (PBI), for which crystallinity was estimated by means of X-ray diffraction measurements [10]. For this polyester, the observed behavior has been attributed to primary and secondary crystallization events, respectively [10]. Accordingly, we can assume that the second period observed in Fig. 10a corresponds to the primary crystallization process during which the crystalline phase induces a drastic reduction in the amount of dipoles involved in the α relaxation. This observation can be explained assuming that additionally to the material immobilized within the crystals there is an extra immobile phase, but not crystalline, that has been referred to as rigid amorphous phase (RAP) [27]. As previously discussed for measurements combining dielectric and X-ray experiments [9,10], one possibility is that this RAP is located between adjacent lamella crystals inside the lamellar stacks. During the primary crystallization process, when the stacks have not impinged with each other, the formation of semicrystalline stacks immobilizes both the amorphous and the crystalline fractions within them. Therefore, the α relaxation observed by dielectric spectroscopy is due essentially to broad amorphous regions between the stacks. This could explain the strong reduction of $\Delta\varepsilon_\alpha$ for moderate increase of X_c^{diel}. For the third period, corresponding to the secondary crystallization, the reduction of $\Delta\varepsilon_\alpha$ becomes inversely proportional to X_c^{diel} with slope ≈ -1. This trend can be explained assuming that during secondary crystallization the segmental immobilization due to the crystallization process is not as effective as in the previous period. In fact, the amount of immobilized material seems to be similar to the amount of material incorporated to the crystals. Again, this interpretation is in agreement with recent results obtained combining dielectric and X-ray techniques [9,10]. As far as PPA is concerned, the data shown in Fig. 10b, refer to the dielectric strength of α, α′ and the addition of both quantities. In this case, the results are more scattered, due to the presence of the two relaxations α and α′ which complicate considerably the data deconvolution procedure. A certain excess of dielectric strength is observed as compared with the data for PPS. It is worth to mention that the conductivity contribution, which may act as a positive background for the ε'' data, cannot be reasonably accounted for because its significant experimental signature is below the lower measured frequency. In spite of that, the presence of different regime is, however, detectable. Quite interestingly, for PPA the second α′ relaxation is observed from the initial stages of the process when X_c^{diel} is still close to 0. Fukao et al. observed by dielectric relaxation and X-ray scattering during isothermal crystallization from the glassy state of poly(ethylene terephthalate) a dynamical transition in the early stage of crystallization [28]. In particular, they reported that the α-relaxation process, associated with the glass transition, was transformed into another relaxation process, α′, before the formation of the crystalline phase. This secondary process, α′, becomes the characteristic segmental relaxation of the semicrystalline polymer at the end of the crystallization process [8,9]. One additional aspect to be discussed is the reason for the appearance of the secondary α′ process in PPA and not in PPS. This can be explained considering that, after completion of the crystallization process, the α relaxation of the semicrystalline PPS sample is about half an order of magnitude slower than the original one (Fig. 6), while for PPA this final segmental relaxation, α′, is about one and a half orders of magnitude slower than the initial one (Fig. 7). This fact provokes that the α′ relaxation for PPS, if present, is merged with the α one. As a consequence, as crystallization proceeds, only one transition can be experimentally observed.

4.2.2. *Early stages of crystallization*

One of the most streaking facts of the crystallization experiments is the existence of a first regime where the $\Delta\varepsilon_\beta$ remains nearly unchanged while a significant decrease of $\Delta\varepsilon_\alpha$ relaxation is observed. This effect was previously discussed for PPS [28]. Considering that $\Delta\varepsilon_\beta$ can be considered to be inversely proportional to the amount of crystalline phase [6] then the first regime can be identified with the induction period of crystallization. The observed decrease of $\Delta\varepsilon_\alpha$ in the induction period indicates a modification of dynamics in the molten state with respect to the initial one. In order to discuss this time dependence, one has to consider the Kirkwood–Fröhlich equation [26] which describes the so called reduced dielectric strength $f(\varepsilon_0)$, defined as:

$$f(\varepsilon_0) = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} = \frac{4\pi\rho N_a}{9kTM} g\mu^2 \tag{6}$$

where g is the correlation factor, ρ is the density, μ is the dipole moment of the relaxing unit, M is the molecular weight of the repeating unit, N_a is the Avogadro's number, and k is the Boltzmann constant. The values for ε_0 and ε_∞ can be obtained from the measured real part of ε^*. In Figs. 8c and 9c, right y-axis, the normalized values of $f(\varepsilon_0)$ have been shown for PPS and PPA, respectively, during the induction period. The net decrease exhibited by $f(\varepsilon_0)$,while $\Delta\varepsilon_\beta$ remains nearly constant, can be interpreted as due to a decrease of the correlation factor induced by an increment of the molecular correlation in the induction period. A qualitatively similar effect has been reported to appear in polymer networks with increasing amount of crosslinks [29]. The observed decrease of $\Delta\varepsilon_\alpha$ in the induction period indicates a modification of dynamics in the molten state with respect to the initial one. There are several possibilities to account for this observation. Among others, the formation of fringed micelle nuclei, as expected when a spinodal liquid–liquid phase separation is present [30,31], or the formation of mobile "baby nuclei", predicted by computer simulation [32], which may act as physical crosslinks somehow pinning most of the amorphous phase and therefore an enhancement of the segmental correlation can be taken into account. Regardless of the model invoked, our results seem to point towards the existence of precursors of crystallization in the induction period.

5. Conclusions

In the present paper, we have shown that by means of dielectric spectroscopy it is possible to follow in a straightforward manner the isothermal polymer crystallization of two model aliphatic polyesters, poly(propylene succinate) (PPS) and poly(propylene adipate) (PPA) measuring simultaneously the α relaxation and the β relaxation. The simultaneous measurement of α and β relaxations allowed us to characterize, by a single experiment, structural development, through the magnitude $X_c^{\text{diel}} = 1 - \Delta\varepsilon_\beta/\Delta\varepsilon_\beta^{\text{o}}$, and dynamics evolution, through $\Delta\varepsilon_\alpha$, during the crystallization process. The results obtained demonstrated the existence of three differentiated regimes for PPS and PPA. In particular, there is firstly an induction period, in which $\Delta\varepsilon_\alpha$ decreases without significant increase of X_c^{diel}, that has been assigned to the induction period for crystallization; then, a second period, in which $\Delta\varepsilon_\alpha$ decreases strongly with X_c^{diel} that has been attributed to primary crystallization; lastly, a third period, in which $\Delta\varepsilon_\alpha$ decreases following an inversely proportionality with respect to X_c^{diel} with slope ≈ -1 that has been related to the secondary crystallization. Additionally, the dielectric measurements performed on the amorphous polymers further support a close relationship between local and segmental dynamics in polyesters as proposed by the coupling model.

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