Molecular dynamics and microstructure development during cold crystallization in poly(ether-ether-ketone) as revealed by real time dielectric and x-ray methods

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The isothermal crystallization process of poly(ether-ether-ketone) from the glass has been studied in real time by dielectric spectroscopy and x-ray scattering experiments. The combination of these two techniques revealed a complete picture of the crystallization processes from the point of view of both amorphous and crystalline phases. Analysis of results shows that the sample morphology consists of lamellar stacks, separated by rather broad amorphous regions. The lamellar stacks are highly crystalline ($\sim 70\%$), as obtained from both dielectric and x-ray scattering measurements, and the amorphous phase within the stacks is constrained up to a level where no segmental relaxation is possible. The remaining amorphous phase, after completion of the primary crystallization process, still has a certain mobility, but it is significantly slower than the initial amorphous mobility. Dielectric data and x-ray results are found to be highly congruent. © 2001 American Institute of Physics. [DOI: 10.1063/1.1388627]

I. INTRODUCTION

When a glassy polymer is heated above its glass transition temperature (T_g), segmental mobility can enhance a large number of conformations in polymer chain segments. In some cases this conformation mobility may initiate the formation of three-dimensional ordered crystallites, which are thermodynamically more stable. However, it is known that, in an assembly of random polymer chains which are coiled and mutually interpenetrated, it is nearly impossible, for purely kinetic reasons, to reach a complete crystalline state.¹ Polymer systems thus always form structures which are partially crystalline. The structure of semicrystalline polymers exhibits characteristic features depending on the length scales. In the 10^{-8} m scale, in highly crystalline polymers, such as polyethylene (PE)² and in intermediate crystalline polymers, such as poly(ethylene-terephthalate) (PET)³ or poly(ether-ketone)s,⁴ there is an alternation between crystalline regions (lamellar crystals) and amorphous regions (interlamellar amorphous regions). With the exception of highly crystalline polymers, this alternation does not extend to the whole volume of the sample.³ The lamellae are packed into stacks which are separated by broad amorphous regions. The stacks can assemble themselves into superstructures, generally with spherical symmetry (spherulites) which can reach

microns or even several millimeters. From the above picture, it is evident that the simple, ideal two-phase model is insufficient to describe the microstructure of the semicrystalline polymer. In this context, the various interactions between the amorphous and crystalline phases allow one to envision the amorphous fraction as a phase of variable properties in the crystalline environment.⁵⁻⁸

X-ray scattering techniques provide information about the structure of the ordered regions at different length scales. Wide angle x-ray scattering (WAXS) offers the possibility to obtain information about molecular ordering on the scale of several angstroms. It is useful to estimate the crystallinity, i.e., the fraction of material which possesses three-dimensional ordering. Small angle x-ray scattering (SAXS), on the other hand, allows one to analyze the structure developed over the length scale of tens of nanometers. Synchrotron radiation further offers the possibility to perform real time SAXS and WAXS experiments simultaneously during crystallization,⁹ which has enhanced the understanding of the correlation between the nanostructure and crystal development.^{10,11} By using both techniques simultaneously, the ordering of the macromolecules through a very broad length scale can be examined.

X-ray scattering techniques in general, however, do not provide direct information about the dynamic processes occurring within the amorphous phase. This is mainly due to the absence of changes in the order or contrast. Dielectric spectroscopy (DS) techniques have been shown to be very valuable when dealing with the dynamics of the amorphous chains.¹²⁻¹⁴ In the present study we have used the combined x-ray and dielectric techniques to get a complete picture of the structural and dynamical changes during crystallization from the glass. In general, the relaxation of partially crystal-

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line polymers is a complex mechanism and it can exhibit different features from that of pure amorphous systems.^{15,16} The reason for these differences is because semicrystalline polymers have a much less homogeneous behavior. The molecular dynamics in semicrystalline polymers has been extensively investigated.^{15,17,18} The α relaxation in semicrystalline polymers, when compared to that of amorphous systems, is broader, less intense, and generally displaced towards higher temperatures.^{5,12–14,16,19} The cooperative character of the α relaxation implies that the molecular motions are correlated up to a certain distance ξ .²⁰ Consequently, the restraints imposed by the crystals become effective over a similar range. However, local relaxations involving the motion of small pendant groups (β relaxation) appear to be less affected by the presence of crystalline regions in the polymer.^{6,7,15} Due to the heterogeneous nature of the structures at different length scales, it is reasonable to expect that amorphous chains located in different regions of the sample will display different dynamics, depending on their environments. The presence of different levels of molecular mobility in the amorphous phase of semicrystalline polymers has been demonstrated by relaxation and calorimetric experiments.^{21–24} These experiments show that there exists a rigid amorphous phase, which either does not relax or only relaxes, well above the glass transition temperature. It is reasonable to assume that the differences in the constraints imposed by the crystals to the amorphous phase will be highly dependent on the structures of the semicrystalline polymer. Hence, in order to better understand how the amorphous regions are confined within crystalline phase, it is necessary to have an in-depth knowledge not only about the crystallinity but also on the polymer structures at different scales (microstructure and nanostructure).

The restrictions imposed by the crystalline regions on the amorphous phase are expected to change during the crystallization process. Here, the segmental dynamics of the amorphous phase is gradually modified by the development of crystalline domains. The influence of crystalline rigid and immobile domains on the amorphous phase is rather strong, especially if one considers that the chains in two phases may be physically connected. However, few experiments have been reported in which the influence of the crystalline phase over the segmental motions in the amorphous phase was studied in real time.^{5–8,25}

The main objective of this work is to seek a better understanding of the changes of the dynamics in the amorphous phase during the development of lamellar structure, by combining real time x-ray scattering and dielectric relaxation experiments. The polymer chosen for this study is poly(ether-ether-ketone) (PEEK), a semirigid thermoplastic polymer from the poly(aryl-ether-ketone) family. PEEK has a relatively high glass transition temperature ($T_g \approx 145^\circ\text{C}$ revealed by DSC)^{26,27} and high melting temperature ($T_m \approx 360^\circ\text{C}$). Therefore, PEEK has a wide range of industrial applications, mainly as the matrix for composites.²⁷ We have selected this polymer for the following reasons:

- (a) Its lamellar structure has been extensively studied by different techniques.^{28–31}

- (b) The α relaxation of the amorphous phase of PEEK is highly sensitive to the degree of crystallization.²⁶
- (c) This polymeric material exhibits a low degree of crystallinity (approximately 30%). The remaining 70% material is amorphous, and then it is a suitable material to study dynamic heterogeneities in this phase.

By combining time-resolved scattering techniques and time-resolved relaxation techniques, a complete description of the changes occurring during crystallization in semicrystalline polymers may be achieved.

II. EXPERIMENT SECTION

A. Materials and techniques

Commercial samples of PEEK grade 450G (ICI, $M_n = 15\,400$, $M_w = 40\,000$) were received in the form of amorphous $100\,\mu\text{m}$ thick film. In order to eliminate any kind of orientation due to the processing procedure, the films were folded and molten, and subsequently quenched below T_g . In this way, isotropic films of $200\,\mu\text{m}$ thickness were obtained. Measurements of the dielectric complex permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) were performed in the 10^{-1} – 10^5 Hz frequency range using a broadband dielectric spectrometer from Novo-control. This system contained a dielectric interface with a Stanford SR830 lock-in amplifier. Films for these experiments were provided with circular gold electrodes (3 cm diameter) obtained by sputtering the metal on both free surfaces. The temperature was controlled by means of a nitrogen gas jet, leading to isothermal conditions within an error of $\pm 0.1^\circ\text{C}$.

Simultaneous measurements of wide- and small-angle x-ray scattering were performed in the A2 Polymer Beamline (Hasylab, Hamburg, Germany). The samples were heated in vacuum (10^{-2} torr) at the same heating rate as in the dielectric experiments. A thin aluminum foil covering the surfaces of the film ensured good thermal contact and homogeneous heating. The temperature was measured by a thermocouple embedded in the sample. The wavelength of the radiation used was $1.5\,\text{\AA}$, with a bandpass of $\Delta\lambda/\lambda = 5 \cdot 10^{-3}$. After reaching the selected crystallization temperature T_c , scattering patterns were recorded every 30 s for the $T_c = 160^\circ\text{C}$ experiment and every 60 s for the $T_c = 155^\circ\text{C}$ experiment. The scattered intensity was, then, corrected for fluctuations in the primary beam and the background. The data acquisition system is based on CAMAC hardware and modulator software.³² The WAXS intensity was collected using a linear position-sensitive detector. The detector is located off the primary beam, which allows the x-ray beam to pass through, traveling through a vacuum tube of 1 m length. The SAXS scattering intensity is collected on a second position-sensitive detector located at the end of the vacuum tube.

B. Dielectric relaxation analysis

The description of the dielectric relaxation in terms of the Havriliak–Negami empirical equation³³ for the dielectric permittivity has been shown to be of great use when dealing with polymeric materials.¹² This formalism gives the following expression for the complex dielectric permittivity:

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

where ε_0 and ε_∞ are the relaxed and unrelaxed dielectric constant value, respectively, τ_{HN} is the central relaxation time, and b and c are parameters which describe the symmetric and asymmetric broadening of the relaxation time distribution function, respectively.

C. Wide angle x-ray scattering analysis

The crystallinity, X_c , was calculated as the ratio between the deconvoluted crystalline contribution, given by the crystal reflections, and the amorphous contribution, which is present in the form of an amorphous halo.^{7,34}

D. Small angle x-ray scattering analysis

The position of the scattering maximum, q_{max} , from the Lorentz-corrected SAXS profile, was used for the calculation of the Bragg's long period, L_B ,

$$L_B = \frac{2\pi}{q_{\text{max}}}, \quad (2)$$

where $q = (4\pi/\lambda)\sin\theta$ is the scattering vector, and 2θ is the scattering angle. L_B represents the average periodicity of the lamellar stack, which corresponds, in that approximation, to the sum of the average thickness of the crystal lamellae, l_c , and of the interlamellar amorphous regions, l_a . However, this method does not readily provide any information about l_a or l_c .

The SAXS data have been analyzed using the correlation function approach by Vonk^{35,36} using the methods described by Strobl and Schenider.³⁷ The electronic density correlation function was calculated from the Fourier transform of the Lorentz-corrected profile. Before Fourier transformation can be carried out, the intensity profile has to be extrapolated to $q=0$ and $q=\infty$. The value at $q=0$ was obtained by an extrapolation between the first usable data point and the origin in the Lorentz-corrected plot. The liquid scattering profile and the finite width of the crystal–amorphous interface were estimated using a modified form of Porod's law,³¹ which was used in the extrapolation to $q=\infty$.

The correlation function is given by

$$\gamma_r(\mathbf{r}) = \mathcal{T}^{-1}[\hat{I}(\mathbf{q})] = \int_V \hat{I} e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q}, \quad (3)$$

where $\hat{I}$ is the integral scattered intensity for a given q . The vector $\mathbf{r}$ refers to position vector of a given scattering center from an arbitrary origin within the sample. The correlation function has been normalized by the invariant Q (total scattered intensity). Therefore, the value of the correlation function $\gamma(r)$ at the origin ($r=0$) is equal to unity [Eq. (3)]. Considering the shape of the typical polymeric crystal lamella, a simplification of the treatment described above is to consider the one-dimensional profile of the electron density function. For a perfect two-phase system of crystal lamella, this one-dimensional electron density profile can be

described by the alternation of regions with electron density equal to $\rho_{\text{amorphous}}$ and regions with density equal to $\rho_{\text{crystalline}}$ ($\rho_{\text{amorphous}} < \rho_{\text{crystalline}}$).

The lamellar variables obtained from this analysis of the scattering data are long period (L), linear degree of crystallinity (X_{cL}), crystalline lamellar thickness (l_c) and amorphous layer thickness (l_a). From the correlation function, it is possible to determine two values for the long period: The first maximum (L_c^M) and twice the value of the first minimum (L_c^m), following the terminology adopted by Santa Cruz *et al.*³ The average linear degree of crystallinity in the lamellar stacks can be determined from the following equation:

$$\frac{B}{L_c^M} = x_1 x_2, \quad (4)$$

where B is the first intercept of $\gamma(r)$ with the abscissa, and x_1 and x_2 are the volume fractions of the two phases, within the lamellar stacks, respectively ($x_1 + x_2 = 1$). The thickness of the two phases can be calculated as $l_1 = x_1 L_c^M$ and $l_2 = x_2 L_c^M$. There has been some controversy in the literature with regard to the assignment of l_1 and l_2 to the crystalline and amorphous phases.^{29,30,38} This controversy is a direct consequence of the fact that, from the correlation function itself it is not possible to extract morphological information unless a given model is invoked.³⁰

If one considers the lamella stacks consisting of an ideal two-phase model, Q can be related to the following morphological variables:³⁹

$$Q = k x_{\text{sph}} x_{\text{st}} x_{cL} (1 - x_{cL}) (\rho_c - \rho_{ila})^2, \quad (5)$$

where k is a calibration constant, x_{sph} is the volume fraction of the spherulites in the material, x_{st} is the volume fraction of lamellar stacks within the spherulite, x_{cL} is the volume crystallinity within the stacks, and ρ_c and ρ_{ila} are the electron densities in the two phases—crystalline and interlamellar amorphous, respectively.

The principles of the subsequent analysis and the evaluation of the correlation function are discussed in detail elsewhere.^{31,40,41} For the data processing in this study, custom software SASDAP⁴² was employed.

III. RESULTS

A. X-ray scattering

Figure 1 shows the real time evolution of the WAXS and SAXS patterns and correlation function of the latter during the crystallization process of an initially amorphous PEEK sample heated at $T = 160^\circ\text{C}$ (that is above the calorimetric T_g of the material). For crystallization times t_c longer than 6 min, in the WAXS pattern, the development of three Bragg maxima is clearly seen. These maxima are located at around $q = 1.32 \text{ \AA}^{-1}$, $q = 1.38 \text{ \AA}^{-1}$, and $q = 1.57 \text{ \AA}^{-1}$, which correspond to the (110), (111), and (200) reflections of the orthorhombic unit cell of PEEK,³⁴ respectively. Figure 2 illustrates the evolution of the crystallinity with the crystallization time for the two temperatures studied. As expected, the degree of crystallinity, X_c , develops according to a typical sigmoidal shape for both temperatures. After an

FIG. 1. Real time evolution of the (a) WAXS and (b) SAXS intensity as a function of q and t_c during a crystallization process at $T = 160^\circ\text{C}$ of initially amorphous PEEK. (c) Real time variation of the correlation function obtained from the SAXS patterns during this same crystallization process.

initial induction time, X_c first increases rapidly and finally levels off for longer times. Preceding studies suggest that the induction time for crystallization (from the glass) is governed by the segmental mobility of the supercooled melt.⁴³ The crystallization process is faster at the higher crystallization temperature. The final value of crystallinity reached is about the same within the error of experiment, for the two crystallization temperatures chosen.

The scattered intensity at small angles (Fig. 1) displays a maximum around $q = 0.06 \text{\AA}^{-1}$ for $t_c > 11$ min at $T_c = 155^\circ\text{C}$ and $t_c > 6$ min at $T_c = 160^\circ\text{C}$, which indicates the formation of a stacking lamellar structure. By applying Bragg's law, a final value of the long spacing $L_b \approx 112$

FIG. 2. (a) Plot of the crystallinity X_c as a function of crystallization time t_c for $(\bullet) T = 155^\circ\text{C}$ and $(\circ) T = 160^\circ\text{C}$. Continuous lines represent the evolution of the invariant obtained for these two crystallization temperatures. (b) Estimated value of the fraction of material incorporated within the lamella stacks during the secondary crystallization as a function of crystallization time. Same symbols as for crystallinity.

$\pm 3 \text{\AA}$ is obtained for both crystallization temperatures.

The invariant (Q) (integrated SAXS intensity after the background and Lorentz corrections) is also presented as a function of t_c in Fig. 2 (continuous lines). Q displays a similar sigmoidal dependence on the crystallization time as the crystallinity.

Figure 1(c) shows the one-dimensional correlation function profiles obtained from the data of Fig. 1(b). The variation of the microstructural parameters L_c^M and L_c^m extracted from the CF is shown in Fig. 3. Both parameters exhibit an initial decrease, corresponding to the rapid initial increase of X_c and Q , and a final leveling off at a prolonged time. The final values obtained for the two temperatures are very similar (slightly lower for the higher temperature). As one may see, the L_c^M value is larger than the L_c^m one, both are different from L_b . As pointed out by Santa Cruz *et al.*,³ this difference is caused by the presence of a distribution of long periods, indicating that the periodicity of the stacks is not perfect.³⁰

The parameters l_1 and l_2 (thickness of the two constituent phases) have been obtained, assuming that the system consists of a lamellar morphology from the analysis of the correlation function. Based on several considerations which will be discussed below, the larger value (l_1) has been assigned to the lamellar thickness (l_c), and the smaller value (l_2) has been designated as the thickness of the amorphous layer (l_a). Both l_c and l_a values are illustrated in Fig. 3(b) for the two studied temperatures. Both values initially decrease and remain almost constant during the rest of the crystallization process (secondary crystallization).

FIG. 3. (a) Dependence of the long spacing calculated from the first maximum of the correlation function (L_c^M) (●) $T=155^\circ\text{C}$ and (○) $T=160^\circ\text{C}$, and from double the position of the first minimum L_c^m , (▼) $T=155^\circ\text{C}$ and (▽) $T=160^\circ\text{C}$ with the crystallization time. (b) Dependence of the thickness of the two phases present on the crystalline stacks. (l_1) (●) $T=155^\circ\text{C}$ and (○) $T=160^\circ\text{C}$, and (l_2); (▼) $T=155^\circ\text{C}$ and (▽) $T=160^\circ\text{C}$ with the crystallization time. Continuous lines are to guide the eye.

B. Real time characterization of the α relaxation by dielectric spectroscopy

Figure 4 shows the real time evolution of the α relaxation followed by dielectric spectroscopy during the crystal-

FIG. 4. Real time evolution of the dielectric loss (a) and the dielectric constant (b) during isothermal crystallization ($T_c=155^\circ\text{C}$) as a function of frequency at selected crystallization times (Calorimetric $T_g=145^\circ\text{C}$).

FIG. 5. Variation of the (a) maximum dielectric loss values ϵ''_{max} , and (b) frequency of maximum loss F_{max} , as a function of crystallization time. $T=155^\circ\text{C}$ (●) and $T=160^\circ\text{C}$ (○). Continuous lines are to guide the eyes.

lization process at $T=155^\circ\text{C}$ (Calorimetric $T_g=145^\circ\text{C}$). The imaginary part of the complex dielectric permittivity, measured for the amorphous PEEK, manifests a maximum centered at $F_{\text{max}}=500\text{ Hz}$. In Fig. 4, the α relaxation of the initially amorphous sample is found to endure some changes as crystallization time increases. On the one hand, there is a strong reduction of the peak height. On the other hand, a shift in the position of the α relaxation is observed, for crystallization times longer than 40 min. (After the 40 min crystallization time, the α relaxation shifts towards lower frequencies.) Similar effects have been obtained for the experiment performed at $T_c=160^\circ\text{C}$, in different time scales. The amplitude of the maximum loss ϵ''_{max} , and the frequency of the maximum loss F_{max} , have been illustrated in Fig. 5 as a function of crystallization time for two different temperatures. The variation rate of both magnitudes is dependent on the crystallization temperature. At $T=160^\circ\text{C}$, ϵ''_{max} starts to decrease from $t_c=0\text{ min}$ and it levels off at $t_c>8\text{ min}$. At $T=155^\circ\text{C}$, ϵ''_{max} initially remains constant, and decreases at $t_c>20\text{ min}$ and finally reaches a plateau at $t_c>60\text{ min}$. A very different trend of changes emerges from the inspection of F_{max} (Fig. 5). At both temperatures, F_{max} remains constant when ϵ''_{max} exhibits a higher rate of variation. Only when ϵ''_{max} reaches its lowest plateau value, F_{max} decreases abruptly.

C. Phenomenological description of the α relaxation

An in-depth analysis of the relaxation curves was performed on the basis of the phenomenological description by Havriliak–Negami.³³ The continuous lines in Fig. 4 represent the best-fit results according to Eq. (1). A conductivity term was included to account for the influence of the conductivity process.^{44–46} The obtained parameters are repre-

FIG. 6. Real time evolution of $\Delta\epsilon$, τ_{HN} , b , c , and $b \cdot c$ parameters during isothermal crystallization processes of PEEK at $T=155^\circ\text{C}$ (●) and $T=160^\circ\text{C}$ (○). Continuous lines are to guide the eyes.

sented in Fig. 6 as a function of the crystallization time. It is noteworthy that there is a strong reduction of the relaxation strength $\Delta\epsilon$ for both temperatures, following a sigmoidal variation. The initial $\Delta\epsilon$ value is higher for the lower crystallization temperature, which is in accordance with the Kirwood–Frölich.^{12,45} The final value of $\Delta\epsilon$ is lower for the lower crystallization temperature.

The variation of the shape parameters shows two main features. First, there is a decrease of the asymmetry of the relaxation when crystallization develops, as indicated by the increase of the c parameter towards the higher possible value, $c=1$. Second, the crystallization process produces a broadening of the relaxation curves, as can be seen by the decrease of the b parameter. Both shape parameters exhibit a sigmoidal profile. Independent of the crystallization temperature, the final shape of the relaxation curves is almost the same, as indicated by the similar final shape parameters. The central relaxation time τ_{HN} , shows some different changes during crystallization. During the period in which the other Havriliak–Negami parameters exhibit main variations due to crystallization, the central relaxation time remains almost constant. Only when all the other parameters reach their final values, τ_{HN} begins a sudden change (the value in fact increase at two different rates, fast in the initial period and slow in the final period).

IV. DISCUSSION

A. Lamellar structure development

After the initial induction period, whose duration depends on the temperature, the crystallization process takes place as indicated by the emerging reflection peaks in the WAXS patterns. The occurrence of these peaks is accompanied by the development of a SAXS maximum. This suggests the formation of a larger scale periodicity corresponding to alternating crystalline and amorphous layers giving rise to lamellar stacks.

The correlation function analysis of the SAXS data provides information about the volume fraction of the phases constituting the lamellar stacks. The linear fraction of the constituting phases in the stacks can be calculated as

$$X^{1L} = \frac{l_1}{l_1 + l_2} \quad X^{2L} = \frac{l_2}{l_1 + l_2}. \quad (6)$$

As pointed out above, the ambiguity of the lamellar thickness determined from the correlation function requires the use of a given model to interpret the SAXS data. The correlation method only yields the thickness values for the constituting phases (l_1 and l_2) rather than defining the crystal lamellar thickness or the amorphous layer thickness (l_c and l_a). We have assigned the larger value l_1 as l_c and the smaller value l_2 as l_a . Our reasons, based on structural considerations, are as follows.

The final mass crystallinity for the samples crystallized at the two selected temperatures $T_c=155^\circ\text{C}$ and $T_c=160^\circ\text{C}$ are approximately 22% determined from WAXS (Fig. 2). Time-resolved structural results from the correlation function analysis [Fig. 3(b)] indicate that, for example for $T_c=155^\circ\text{C}$, the final value of l_1 is 87 Å and that of l_2 is 27 Å. This result suggests that the linear crystallinity (within the lamellar stacks) is either ($X_{cL}=l_1/(l_1+l_2)$) 75% or ($X_{cL}=l_2/(l_1+l_2)$) 25%. The assignment of $X_{cL}=25\%$ does not seem appropriate, since it has been demonstrated that for PEEK^{29,47} and for other polymers displaying low degrees of crystallinity (PET, Ref. 3), the morphology consists of lamellar stacks separated by larger amorphous gaps. The assignment of $l_c=l_2$ would lead to a linear crystallinity within the stacks similar to the overall crystallinity. Although examples of this assignment can be found in the literature,^{23,28,48} we will demonstrate below that the dielectric results obtained can only be explained by assuming the first assignment (i.e., $l_c=l_1$).

Let us denote the overall crystallinity in the sample as³⁹

$$X_c = X_s \cdot X_L \cdot X_{cL}, \quad (7)$$

where X_s is the fraction of material included in the spherulites, X_L is the fraction of the material in the lamellar stacks, and X_{cL} is the fraction of the crystalline material in the stacks. As mentioned above, X_{cL} can be estimated as the ratio between the lamellar thickness and the long spacing. From Fig. 3(b), one observes that during the latest stages of primary crystallization (the end of the rapid increase in X_c and Q) the linear fractions of each phase remain nearly constant. This indicates that the composition of the stacks is virtually the same during late stages of the crystallization

process. Similar results have been obtained by Ivanov *et al.*⁴⁹ This implies, according to Eq. (7), that the increase observed in crystallinity during the late stages of crystallization ought to be assigned to an increase in the total amount of the lamellar stacks. When primary crystallization ends, the spherulites are filled in the whole sample, and $X_s = 1$. A rough estimation of X_L at this stage can be obtained through Eq. (7), by considering the final values for X_c , l_1 , and l_2 in Figs. 2(a) and 3(b), respectively. The obtained values are considered to be an approximation, since the parameters X_c and X_{cL} calculated in the way described above have different implications. This is because X_c is obtained from the WAXS patterns (it is a mass fraction); X_{cL} is calculated from the ratio of linear thicknesses (it is a volume fraction). However, the volume fraction is related to the mass fraction by the ratio between the crystal density and the stacking density. The density of completely amorphous PEEK is $\rho_a = 1.294 \text{ g cm}^{-3}$ and that of a 100% crystalline PEEK sample is $\rho_c = 1.364 \text{ g cm}^{-3}$.⁴⁹ Considering these values, the maximum difference between the volume and mass crystallinity would be less than 2.5%. The maximum correction factor would correspond to a mass crystallinity of 50%. Since the fraction of crystalline material in the stacks is very high (around 70%), the differences between mass and volume crystallinities are around 2%. The evolution of X_L value with crystallization time during the secondary crystallization regime is shown in Fig. 2(b). As one can see, for the two selected temperatures a value of X_L of about 0.30 is found, and it presents a slight linear variation with the logarithm of the crystallization time, in favor of our argument about an increase in crystallinity due to an increase in the amount of the stacks. We note that this evidence ($l_1 = l_6$), although subtle, may be real. The strong indication that $l_1 = l_6$ is discussed by combining the dielectric and the scattering results.

B. Correlation between the amount of mobile material and the structural parameters

According to the Kirwood–Frölich equation, the dielectric strength $\Delta\epsilon$ is proportional to the amount of dipoles involved in the relaxation process.¹² The decrease of $\Delta\epsilon$ observed in Fig. 6 hence indicates that, as a consequence of the crystallization process, the amount of relaxing dipoles decreases. This is evident, as the molecules incorporated to the crystals cannot relax. By comparing the evolution of $\Delta\epsilon$ with that of the crystallinity X_c , during the real time crystallization experiments, it is possible to extract valuable information related to the molecular dynamics in different amorphous regions between the crystals. If one considers the normalized value $\Delta\epsilon(\Delta\epsilon^{\text{nor}})$ as a measure of the relaxing material, one can represent its dependence as a function of the amount of crystalline material (Fig. 7). $\Delta\epsilon^{\text{nor}}$ follows a linear dependence with crystallinity. Should the only immobile material be the only one incorporated within the crystals, then the slope of the $\Delta\epsilon - X_c$ linear dependence should be about -1 . However, as one can see in Fig. 7, the dependence is stronger (~ -1.5), showing a faster decrease in $\Delta\epsilon$ as X_c increases. This trend indicates that the growing crystals immobilize not only the material incorporated within them, but also constrain some additional amorphous material, which is

FIG. 7. Normalized value of $\Delta\epsilon$ as a function of the crystalline fraction in PEEK for two selected temperatures. (●) $T = 155^\circ\text{C}$ and (○) $T = 160^\circ\text{C}$.

probably located adjacent to the crystals. Then, it is possible to conclude that not all the noncrystalline fraction behaves as a relaxing material. There is, indeed, an amount of material that does not contribute to the WAXS patterns and that is not relaxing, as evidenced in the dielectric spectroscopy experiments. Such a fraction turns out to be similar for both crystallization temperatures (Fig. 7). As a consequence of this effect, one may predict that on the basis of Fig. 7, a sample with crystallinity higher than 70% would not present any α relaxation, even if it would have an amorphous phase of about 30%. In this regard, early studies from Tidy and Williams⁸ said that the dielectric relaxation strength of the α process was less than expected on the basis of the crystallinity values on semicrystalline polymers, which confirm the existence of a rigid component in the amorphous regions.

Let us recall that our SAXS results could be interpreted in the light of a structural model in which, in the sample filled up with spherulites, the lamellar stacks are separated from each other by larger amorphous gaps. Based on this model, the following argument can be made. Two distinct amorphous regions are present in the model: (a) The interlamellar amorphous phase, which can be visualized as being highly constrained, and (b) the amorphous regions between the lamellar stacks that are less constrained. Considering this scenario, one must include two relaxation processes, one relaxation coming from the restricted interlamellar regions and another relaxation from the interstack amorphous regions. Several authors have proposed this model.⁴⁹ However, our dielectric results do not support the argument of two relaxation processes. Instead, we observe a single relaxation process that changes with crystallization time, and shifts to lower frequencies as secondary crystallization develops (Fig. 4). In addition, the double relaxation model does not provide any explanation for the fraction of the material “invisible” to structural and relaxation techniques, i.e., the *rigid amorphous phase* that we detect.

Let us consider, nevertheless, the amorphous phase between the lamellae. We believe that inside the stacks the noncrystalline chains are constrained to a level where the

FIG. 8. Scheme summarizing the obtained results from SAXS and dielectric spectroscopy. Before crystallization, the polymer chains present segmental motion (schematically depicted by the curved arrows) leading to the dielectric α relaxation. During primary crystallization, the restrictions imposed by the crystalline lamella (represented by the gray domains) mainly inhibit segmental motions within the intralamellar amorphous phase, but not in the interlamellar amorphous phase. During secondary crystallization, the amorphous material located outside the stacks, is able to undergo segmental movement, but its dynamics is slowed down with respect to the purely amorphous phase.

segmental mobility is completely inhibited due to the presence of tightly packed crystals. One may consider the lamellar stacks as “immobile” from the point of view of the dielectric experiments. If this is the case, then $\Delta\epsilon^{\text{nor}}$ represents the fraction of material outside the stacks, i.e., $\Delta\epsilon^{\text{nor}} = 1 - X_L$. Introducing this relationship in Eq. (7), it follows

$$X_c = X_s \cdot X_{cL} (1 - \Delta\epsilon^{\text{nor}}) = X_s \cdot X_{cL} - X_s \cdot X_{cL} \cdot \Delta\epsilon^{\text{nor}}. \quad (8)$$

When the material is fully covered by spherulites, $X_s = 1$. In addition, the extrapolation performed in Fig. 7 ($\Delta\epsilon^{\text{nor}} = 0$), Eq. (8) leads to

$$X_c(\Delta\epsilon^{\text{nor}} = 0) = X_{cL}. \quad (9)$$

From Eq. (9) and Fig. 7 we can calculate that $X_{cL} \approx 70\%$, which is consistent with the value estimated by assuming $l_1 = l_c$ ($X_{cL} = 75\%$). It is convenient to remember that the linear crystallinity obtained (Fig. 7) is a mass fraction, since the X_c values used (from WAXS) are a mass fraction. However, the value obtained from SAXS is a volume fraction. But, as mentioned above, given the crystalline and amorphous densities of our samples, the difference between volume and mass crystallinity is small (below 2%).

In summary, the noncrystalline material included in the lamellar stacks does not contribute to the dielectric α -relaxation process. Based on this assumption the linear crystallinity within the stacks can be calculated, and a value similar to the one calculated from morphological measurements is obtained which supports the interpretation of SAXS results. Figure 8 depicts this situation schematically. In this figure, we assume that the noncrystalline regions in the primary lamellar stacks do not exhibit a relaxation process. Only the noncrystalline regions in the gaps between the stacks show a heterogeneous relaxation behavior, which is strongly dependent of the secondary crystallization process, as we discuss below.

C. Influence of the structure on the α relaxation

As pointed out above, the crystallization process strongly affects the amount of material involved in the relaxation process. An interesting factor to consider is the characteristics of the relaxation process of the remaining mobile material. As observed in Fig. 5, the position of the relaxation function does not change during the primary crystallization, where there are major changes in the crystallinity. Considering $(2\pi F_{\text{max}})^{-1}$ as an average relaxation time, the observed decrease in F_{max} at longer crystallization times indicates that there is a slowing-down tendency of the chain mobility as the crystals develop further. However, this decrease does not occur until the sigmoidal parameters reach their final plateau values. The dynamics of the amorphous material during the crystallization process is affected by the primary crystallization as long as the corresponding relaxation curve is broadened and gradually becomes symmetric. This fact suggest that low frequency contributions are coming in, and they may arise from the influence of the crystalline regions. The limit of such an influence would be to suppress completely the motions, enhancing the appearance of a rigid amorphous content. The relaxation process remains, however, at the same rate, as indicated by the similar F_{max} . On the other hand, the secondary crystallization strongly affects the dynamics of the remaining amorphous phase, slowing down the relaxation, and consequently diminishing the frequency of the maximum loss, F_{max} .

Concerning the shape of the relaxation, the appearance of the crystallinity modifies the shape parameters almost from the very beginning, especially the case for the broadening parameter b . As one can see in Fig. 6, the variation of b is parallel to the variation of crystallinity. To emphasize this effect, the variation of the shape parameters with crystallinity is illustrated in Fig. 9. On the one hand, b , which is related to the long-range modes of the relaxation process,¹⁹ decreases gradually with crystallinity [Fig. 9(a)]. This indicates that the presence of a small amount of crystals is enough to affect the long-range modes. On the other hand, according to the Schönhals and Schlösser (SS) model, the product of $b \cdot c$ is related to the short-scale modes of the relaxation process. These modes are apparently not affected by the crystallinity, as they belong to local movements [Fig. 9(b)]. Another important feature in Fig. 9 is that, with independence of the crystallization temperature, both shape parameters behave exactly the same. The case for τ_{HN} is different [Fig. 9(c)]. As crystallinity starts to increase, the relaxation time remains unaffected. Only when the crystallinity achieves a certain critical value ($X_c \sim 0.15$), the relaxation time begins to increase, indicating a slowing down of the mobility of the unrestricted amorphous fraction. This critical value is the same for both temperatures investigated in this study. A possible explanation for this effect could be the following.

During primary crystallization, the formation of lamellar stacks produces an immobilization, not only of the material incorporated into the crystals, but also of the amorphous material remaining between lamella crystals. This fact strongly influences $\Delta\epsilon$, since it is related to the amount of the dipoles involved in the relaxation process. It also affects the shape of

FIG. 9. Variation of the relaxation shape parameters b and $b \cdot c$, and the relaxation time τ_{HN} as a function of crystallinity. (●) $T = 155^\circ\text{C}$ and (○) $T = 160^\circ\text{C}$.

the relaxation process, as the long-range motions are hindered due to the presence of crystals. As primary crystallization develops, the b parameter decreases and the c parameter increases. The relaxation becomes broader and more symmetric, due to the increasing number of different environments created by the crystals. However, this situation does not affect the position of the relaxation peak. The average relaxation time of the remaining relaxing areas (broad amorphous areas located between the lamellar stacks) is the same. Once the space is filled in with spherulites, the only location where the system can continue crystallizing is in the broad gaps between the stacks. The remaining amorphous phase located in these areas has similar or slightly restricted mobility as compared to the initial amorphous sample. Secondary crystallization has the effect of restricting the mobility on these amorphous gaps. As a consequence, the average relaxation time is now increased. Within this context, recent works have invoked the occurrence of fringed micelle-like crystals between different lamellae.^{50,51} Our results indicate that, if those crystals exist, they could not grow in between the lamellae within the stacks. They would have to develop in between lamellar stacks, where the amorphous phase is also constrained, but a certain degree of molecular mobility, necessary to form those crystals or any other kind of crystals, still prevails.

From the above scenario, it can be inferred that the simplistic description of two different relaxation processes within the remaining amorphous phase would not be enough. Moreover, in the amorphous phase of the semicrystalline polymer there is a grading of the α process between the “normal amorphous phase” and the “fully rigid amorphous phase.”

V. CONCLUSIONS

The combination of real time techniques revealing the parallel evolution of the crystalline phase (WAXS and SAXS) together with methods detecting the real time changes in the amorphous phase (dielectric spectroscopy), shows an in-depth and complete picture of crystallization processes from the glass in PEEK. The obtained results support the concept that sample morphology consists of lamellar stacks, separated by broad amorphous regions. The composition of the lamellar stacks is highly crystalline, as obtained from both dielectric and structural x-ray measurements (around 70%) and the amorphous phase inside the stacks is constrained up to a level where no segmental relaxation is possible. After completion of the primary crystallization process, the remaining amorphous phase has a certain mobility, but it is significantly slowed down by the event of secondary crystallization.

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¹G. Strobl, *The Physics of Polymers* (Springer, Berlin, 1996).

²B. Wunderlich, *Macromolecular Physics* (Academic, New York, 1973), Vol. 1.

³C. Santa Cruz, N. Stribeck, H. G. Zachmann, and F. J. Baltá-Calleja, *Macromolecules* **24**, 5980 (1991).

⁴D. C. Bassett, R. H. Olley, and A. Raheil, *Polymer* **33**, 3971 (1988).

⁵T. A. Ezquerra, J. Majszczyk, F. J. Baltá Calleja, E. López Cabarcos, K. H. Gardner, and B. S. Hsiao, *Phys. Rev. B* **50**, 6023 (1994).

⁶T. A. Ezquerra, F. J. Baltá Calleja, and H. G. Zachmann, *Polymer* **35**, 2600 (1994).

⁷A. Nogales, T. A. Ezquerra, J. M. García, and F. J. Baltá Calleja, *J. Polym. Sci., Part B: Polym. Phys.* **37**, 37 (1999).

⁸G. Williams, *Adv. Polym. Sci.* **33**, 59 (1979).

⁹C. Wutz, M. Bark, J. Cronauer, R. Döhrmann, and H. G. Zachmann, *Rev. Sci. Instrum.* **66**, 1303 (1995).

¹⁰H. G. Zachmann and R. Gehrke, in *Morphology of Polymers*, edited by B. Sedlacek (Gruyter, New York, 1986).

¹¹M. Bark and H. G. Zachmann, *Acta Polym.* **44**, 18 (1993).

¹²P. Hedvig, *Dielectric Spectroscopy of Polymers* (Hilger, Bristol, England, 1977).

¹³N. G. McCrum, B. E. Read, G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (Dover, New York, 1991; Original Issue Wiley, London, 1967).

¹⁴*Dielectric Spectroscopy of Polymeric Materials: Fundamentals and Appli-*

- cations, edited by J. P. Runt and J. J. Fitzgerald (ACS, Danvers, MA, 1997).
- ¹⁵J. C. Coburn and R. H. Boyd, *Macromolecules* **19**, 2238 (1986).
 - ¹⁶C. R. Ashcraft and R. H. Boyd, *J. Polym. Sci.* **14**, 2153 (1976).
 - ¹⁷J. Dobbertin, A. Hensel, and C. Schick, *J. Therm. Anal.* **47**, 1027 (1996).
 - ¹⁸D. S. Kalika and R. K. Krisnaswamy, *Macromolecules* **26**, 4542 (1993).
 - ¹⁹E. Schlösser and A. Schönhals, *Colloid Polym. Sci.* **267**, 963 (1989).
 - ²⁰E. J. Donth, *J. Non-Cryst. Solids* **53**, 325 (1982).
 - ²¹K. N. Krüger and H. G. Zachmann, *Macromolecules* **26**, 5202 (1993).
 - ²²S. Z. D. Cheng, Z. Q. Wu, and B. Wunderlich, *Macromolecules* **20**, 2802 (1987).
 - ²³P. Huo and P. Cebe, *Macromolecules* **25**, 902 (1992).
 - ²⁴P. Huo and P. Cebe, *J. Polym. Sci., Part B: Polym. Phys.* **30**, 239 (1992).
 - ²⁵I. Sics, A. Nogales, T. Ezquerra, Z. Denchev, F. J. Baltá-Calleja, A. Meyer, and R. Döhrmann, *Rev. Sci. Instrum.* **71**, 1733 (2000).
 - ²⁶A. Nogales, T. A. Ezquerra, F. Batallán, B. Frick, E. López Cabarcos, and F. J. Baltá Calleja, *Macromolecules* **32**, 2301 (1999).
 - ²⁷H. H. Kausch, *Advanced Thermoplastic Composites* (Hanser, Munich, 1993).
 - ²⁸C. Fournies, P. Damman, M. Dosiére, and M. H. Koch, *Macromolecules* **30**, 1392 (1997).
 - ²⁹B. S. Hsiao, B. B. Sauer, R. K. Verma, H. G. Zachmann, S. Seifert, B. Chu, and P. Harney, *Macromolecules* **28**, 6931 (1995).
 - ³⁰R. K. Verma, H. Marand, and B. S. Hsiao, *Macromolecules* **29**, 7767 (1996).
 - ³¹B. S. Hsiao and R. K. Verma, *J. Synchrotron Radiat.* **5**, 23 (1997).
 - ³²C. Boulin, R. Kampf, M. H. J. Koch, and S. M. McLaughlin, *Nucl. Instrum. Methods Phys. Res. A* **249**, 399 (1986).
 - ³³S. Havriliak and S. Negami, *Polymer* **8**, 161 (1967).
 - ³⁴D. J. Blundell and B. N. Osborn, *Polymer* **24**, 953 (1983).
 - ³⁵G. Kortleve and C. G. Vonk, *Kolloid Z. Z. Polym.* **225**, 124 (1968).
 - ³⁶C. G. Vonk and G. Kortleve, *Kolloid Z. Z. Polym.* **220**, 19 (1967).
 - ³⁷G. R. Strobl and M. Schneider, *J. Polym. Sci.* **18**, 1343 (1980).
 - ³⁸A. M. Jonas, T. P. Russell, and D. Y. Yoon, *Macromolecules* **28**, 8491 (1995).
 - ³⁹H. G. Zachmann and C. Wutz, in *The Crystallisation of Polymers*, edited by M. Dosiére (Kluwer Academic, Dordrecht, 1993), p. 403.
 - ⁴⁰J. T. Koberstein, B. Morra, and R. S. Stein, *J. Appl. Crystallogr.* **13**, 34 (1980).
 - ⁴¹F. J. Baltá-Calleja and C. G. Vonk, *X-ray Scattering of Synthetic Polymers* (Elsevier Science, New York, 1989).
 - ⁴²The SASDAP software (*Small Angle Scattering Data Analysis Program*) is written by R. Verma in collaboration with A. Biswas and B. S. Hsiao (Central Research and Development, DuPont Experimental Station, Wilmington, DE).
 - ⁴³A. Nogales, T. A. Ezquerra, Z. D. Denchev, and F. J. Baltá Calleja, *Polymer* **42**, 5711 (2001).
 - ⁴⁴K. U. Kirst, F. Kremer, and V. M. Litvinov, *Macromolecules* **26**, 975 (1993).
 - ⁴⁵C. J. Bottcher, *Theory of Electric Polarization* (Elsevier, New York, 1992).
 - ⁴⁶M. Antonietti, M. Meskos, F. Kremer, and G. Blum, *Acta Polym.* **47**, 460 (1996).
 - ⁴⁷A. J. Lovinger, S. D. Hudson, and D. D. Davis, *Macromolecules* **25**, 1752 (1992).
 - ⁴⁸A. Jonas and R. Legras, *Macromolecules* **26**, 813 (1993).
 - ⁴⁹D. A. Ivanov, R. Legras, and A. M. Jonas, *Macromolecules* **32**, 1582 (1999).
 - ⁵⁰A. Alizadeh, L. Richardson, J. Xu, H. Marand, W. Cheung, and S. Chum, *Macromolecules* **32**, 6221 (1999).
 - ⁵¹H. Marand, A. Alizadeh, R. Farmer, R. Desai, and V. Velikov, *Macromolecules* **33**, 3392 (2000).