Restricted Dynamics in Poly(ether-ether-ketone) as revealed by
Incoherent Quasielastic Neutron Scattering and Broad Band
Dielectric Spectroscopy.

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Abstract

The molecular dynamics of semicrystalline poly(ether-ether-ketone) (PEEK) was studied over a broad dynamic range from 10^{-1} Hz to 10^9 Hz by combining dielectric spectroscopy (DS) and incoherent quasielastic neutron scattering (IQNS). This allowed us to characterize the polymer dynamics in the glassy, semicrystalline and molten state. By performing dielectric and neutron scattering measurements in a comparable frequency range it was proved that the quasielastic broadening observed in IQNS experiments corresponds to the dielectric α relaxation without invoking any kind of low frequency dielectric data extrapolation. IQNS measurements indicate that the segmental chain motion observed at temperatures higher than the glass transition temperature possesses an elastic and a quasielastic contribution. A model which considers a confined jump diffusive motion allows a quantitative description of the IQNS spectra. This model provides dimensions of jump length, residence time, available space and number of scatterers involved in the process. Results indicate that, both, the size of the restricted volume and the amount of protons involved in the α process increase with temperature and are smaller than the calculated ones on the crystallinity estimates from calorimetric and X-ray diffraction experiments. Both effects indicate for semicrystalline PEEK the existence of a confined amorphous

phase with regions of different degrees of mobility. The present experiments provide a quantitative dynamical and spacial description of the heterogeneous amorphous phase of semicrystalline PEEK.

1 Introduction

The microstructure of semicrystalline polymers typically displays a distinct morphology consisting of laminar crystals intercalated by less ordered regions. The distribution of the crystalline regions may give rise to the appearance of different textures [1]. It is known that the dynamics of the amorphous phase in semicrystalline polymers presents characteristic features which differ from those observed in pure amorphous polymers [2]. In particular, at temperatures higher than the glass transition temperature (T_g), polymer chain segments in the amorphous regions are restricted to move between the crystals [2, 3]. This confinement broadens the glass transition region and shifts T_g towards higher values [4]. Above T_g , the confinement effects are reflected in the dielectric α relaxation provoking a decrease of the dielectric strength, an increase of the central relaxation time, τ , and a broadening of the relaxation process [2, 3, 5]. The dynamics of the amorphous phase in a semicrystalline polymer can be envisioned as a result of a process of self-confinement within the restricted geometry imposed by the crystalline regions as crystallinity develops. A strong interaction between the amorphous phase and the crystalline interphase is expected as polymer chains in the former are physically connected with the crystals. Relaxation and calorimetric experiments in semicrystalline polymers reveal the existence, above T_g , of different levels of mobility in the amorphous regions. In

particular, the existence of a rigid amorphous phase (RAP) which does not relax or only relaxes partially well above T_g has been proposed [6, 7, 8, 9, 10, 11]. The location of the RAP in the crystal-amorphous interphase or as an independent phase still is an open question.

In addition to dynamic mechanical analysis and dielectric spectroscopy, incoherent neutron scattering experiments are valuable when dealing with polymer dynamics. On the one hand, the possibility of measuring the energy transfer between the neutron and the polymer allows one to study polymer dynamics above and below T_g . On the other, from the dependence of the incoherent scattered intensity on the momentum transfer (Q), information about the geometrical characteristics and length scale of the molecular motion can be inferred [12, 13].

Poly(ether-ether-ketone) [14] (PEEK), is a semirigid polymer which can be crystallized either from the melt or from the glassy state. PEEK has been extensively studied and it is known that its crystals are arranged in a spherulitic morphology when crystallized from the melt or from the glassy state at temperatures lower than 573 K [15, 16, 17]. Spherulites consist of dense lamellar stacks of crystals and amorphous pockets or gaps between and within them [18, 15]. The existence of a rigid amorphous phase in this polymer has been demonstrated by means of several techniques [9, 10, 19, 20]. However, there is still

some controversy about the degree of mobility of the RAP in the range between T_g and T_m [9, 10]. Dielectric experiments have shown an increase of the dielectric strength of the α relaxation [10] with temperature pointing towards a progressive mobilization of the RAP.

In the present study the relaxation process of the amorphous phase of PEEK confined within their own crystals is analyzed over a broad dynamic range above T_g by combining dielectric spectroscopy and incoherent quasielastic neutron scattering (IQNS). The aim of the work is to present a quantitative dynamical and spacial description of the heterogeneous amorphous phase of semicrystalline PEEK.

2 Experimental Part

2.1 Materials

The polymer investigated was a PEEK 450 G from ICI in the form of amorphous films with a thickness of $\approx 50\mu\text{m}$. This sample has a number average molecular weight of $M_n = 12500$ g/mol and a weight average molecular weight of $M_w = 40000$ g/mol. The glass transition temperature of the amorphous sample, as measured by differential scanning calorimetry (DSC) is 418 K. The chemical structure of the repeating unit is shown in the inset of fig. 1.

2.2 Techniques

DSC experiments were carried out with a Perkin-Elmer DSC7 equipment at a heating rate of 20K/min. The temperature was calibrated by using Indium and Zinc standards. The samples were encapsulated in aluminum pans and the typical sample weights used in these experiments were of about 7mg.

Measurements of the complex dielectric permittivity, $\epsilon^* = \epsilon' - i\epsilon''$, were performed over a broad frequency window, $10^{-1}\text{Hz} < F < 10^8 \text{ Hz}$, in a temperature range of $123\text{K} < T < 423\text{K}$. To cover the above frequency range, three different experimental setups were used. From 10^{-1}Hz to 10^5Hz a Novocontrol system integrating a SR 830 Lock-in amplifier with a dielectric interface was employed. In the range 10^6Hz - 10^8Hz , dielectric measurements were obtained by means of a HP 4291 coaxial line reflectometer. In this case, the complex permittivity was calculated by measuring the reflection coefficient at a particular reference plane [21]. These two equipments were integrated in a Novocontrol broadband dielectric spectrometer. The temperature in this spectrometer is controlled by a nitrogen jet with a temperature error, during every single sweep in frequency, of $\pm 0.1 \text{ K}$. The frequency gap from 10^5Hz to 10^6Hz was covered by using a HP 4192 impedance analyzer. Dielectric measurements in this frequency range were performed by using a home made cryostat operating on at a temperature controlled nitrogen atmosphere. Owing to the fact that two different cryostats

were used, the measuring temperatures do not completely coincide. In order to obtain the whole isothermal curve the ϵ'' values in the 10^5Hz - 10^6Hz were interpolated between two consecutive isothermal measurements performed with the HP 4192. Circular gold electrodes were sputtered onto the free surfaces of the films with a diameter of 3 cm for the measurements up to 10^6Hz and 0.5 cm for measurements at $F > 10^6\text{Hz}$.

The phenomenological Havriliak-Negami(HN) [22] formulation was used to describe the dielectric α relaxation. In this approach, the complex dielectric permittivity exhibits a frequency (ω) dependence of the form:

$$\epsilon^* = (\epsilon_\infty) + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (i\omega\tau_0)^b]^c} \quad (1)$$

where ϵ_0 and ϵ_∞ are the relaxed($\omega = 0$) and unrelaxed($\omega = \infty$) dielectric constant values, τ_0 is the central relaxation time of the relaxation time distribution function and b and c ($0 < b, c < 1$) are shape parameters which describe the symmetric and the asymmetric broadening of the relaxation time distribution function, respectively [22]. Eq. 1 leads to the a Debye single relaxation time equation when $b=c=1$. In semicrystalline polymers there appears an enhanced contribution to ϵ'' at low frequencies which is attributed to the polarization of the crystal surface [2]. Therefore, to analyze the shape and temperature evolution of the α relaxation a conduction term was included in eq. 1 as $\sigma/(\epsilon_{vac}\omega^s)$,

were σ is related to the direct current electrical conductivity, ϵ_{vac} is the vacuum dielectric constant and s is related to the nature of the conduction mechanism. A value of $s < 1$ is related to a non-ohmic transport [23].

Neutron scattering measurements were carried out at the neutron backscattering spectrometer IN10, at the Institute Laue-Langevin (ILL) in Grenoble, France. This spectrometer allows one to look for dynamics around 10^{-9} s. The incident neutron wavelength was $\lambda = 6.27 \text{ \AA}$. The experimental Q -range of the instrument was $0.4 \text{ \AA}^{-1} < Q < 2.0 \text{ \AA}^{-1}$ where Q is the momentum transfer defined by $Q = (4\pi/\lambda)\sin(\theta)$ being 2θ the scattering angle. Two series of measurements were performed at several Q -vectors covering the whole Q -range of the instrument. In the first series a temperature range between 4K and 400K was covered by using a cryofurnace. In the second series a range between 300K and 700K was covered using a furnace. The quasielastic measurements were performed by varying the monochromator position with a mechanical Doppler driver which provides an experimental energy window of $-14 \mu\text{eV} < E < 14 \mu\text{eV}$. Quasielastic spectra were recorded at selected temperatures for every Q . Accumulation times of 12 hours for $T < 550\text{K}$ and 24 hours for $T > 550\text{K}$ were typically used. The samples were either hollow cylinders of 3 cm in diameter or flat square specimens (3.4 cm^2). The thickness of the sample was selected to yield a transmission of about 90%. The experimental resolution was obtained

from a measurement performed at 4K, were it was assumed that no molecular motion occurs. Standard correction programs of ILL were used to subtract the scattering from the empty cell and spectrometer and to correct for detector and analyzer efficiency, as well, as for selfscreening and absorption of the sample.

The incoherent scattering cross section of hydrogen is very large in comparison with the coherent and incoherent cross sections of other atoms such as carbon and oxygen. Accordingly, for PEEK, the ratio between σ_{inc} for hydrogen and the total scattering cross section, σ_t , is of about 0.87. Thus, measurement of the incoherent scattering function for the hydrogen atoms of the polymer provides information about the dynamics of the polymeric chains. For the analysis of our experimental data we consider the molecular motion formed by the combination of a vibrational motion and a relaxation process. In this case, assuming that the vibrational and the relaxation motions are uncoupled and provided that the inelastic contribution appears well separated from the quasielastic one, the incoherent scattering function $S_{inc}(Q, \omega)$ can be described by [12, 24, 25]:

$$S_{inc}(Q, \omega) = S_{inc}^{vib}(Q, \omega) \otimes S_{inc}^{rel}(Q, \omega) \quad (2)$$

where $\otimes$ means the convolution product in ω and $S_{inc}^{vib}(Q, \omega)$ is the incoherent scattering function of the vibrational motion which corresponds to the elas-

tic Debye-Waller factor. For the relaxation process, the quasielastic function $S_{inc}^{rel}(Q, \omega)$ is given by a quasielastic contribution and an elastic component in the following way:

$$S_{inc}^{rel}(Q, \omega) = A_0(Q) \cdot \delta(\omega) + [1 - A_0(Q)] \cdot L(\omega, \Gamma(Q)) \quad (3)$$

where $L(\omega, \Gamma(Q))$ is a relaxation function with a half width at half maximum (HWHM) $\Gamma(Q)$ and $A_0(Q)$ is the Elastic Incoherent Scattering Function (EISF). For the data treatment, a convolution of $S_{inc}(Q, \omega)$ with the experimental resolution was made. From the fit with the experimental results $A_0(Q)$ and $L(\omega, \Gamma(Q))$ were obtained. In a second step, more specific models for the Q -dependence of $A_0(Q)$ and $\Gamma(Q)$ are proposed to obtain the geometrical parameters of the dynamics.

3 Results

3.1 Differential Scanning Calorimetry

Fig. 1 shows the DSC traces of a semicrystalline PEEK specimen (a) and an amorphous PEEK film (b). The glass transition for the amorphous sample manifests itself by a jump in the heat flow at $T_g=418\text{K}$. Upon heating at 20K/min a sharp exotherm appears, indicating the cold crystallization of amor-

phous PEEK. The crystallization temperature measured at the minimum of the exotherm is 448K. At higher temperatures an endothermic peak centered around 613K evidences the melting of the PEEK crystals. The thermal history of the semicrystalline sample was chosen to reproduce the one followed in the IQNS experiments. The sample was crystallized from the glassy state by heating at 1.5 K/min, in three temperature steps of 50K starting at 400K (450K, 500K and 550 K respectively). At each temperature the sample was held isothermally for 7 hours. After the final treatment at 550K the sample was cooled down to room temperature. The corresponding DSC experiment of this sample (trace (a), fig. 1) shows a shift towards higher values of the T_g and a smaller jump at the glass transition as compared with the amorphous one. The magnitude of this jump is proportional to the amount of material which relaxes at the glass transition defined by $X_a = (\Delta C_p)^{sc} / (\Delta C_p)^a$. Here, $(\Delta C_p)^{sc}$ and $(\Delta C_p)^a$ are the the heat capacity increments at T_g for the semicrystalline and amorphous sample respectively. At higher temperature, two endothermic peaks are present which correspond to the melting of two population of crystal lamellae. The low temperature one can be associated to the melting of secondary lamellae while the high temperature endotherm is attributed to the melting of primary lamellae [15]. The amount of crystalline material, X_c , can be calculated from the area of the melting endotherm assuming for the melting

enthalpy of the 100% crystalline PEEK a value of 130 J/g [26]. According to previous studies of this polymer [9], ΔC_p is not exclusively proportional to the amorphous weight fraction $(1-X_c)$. The amount of amorphous material which remains immobile beyond the glass transition temperature (X_{RAP}) can be estimated from the ΔC_p measurement by $X_{RAP}=1-X_c-X_a$. In our case, for the semicrystalline sample, values of $X_c \approx 0.34 \pm 0.01$, $X_a \approx 0.48 \pm 0.06$ and then $X_{RAP} \approx 0.18 \pm 0.07$ are derived. These values are in qualitative agreement with previous reported values [9]

3.2 Broad Band Dielectric Spectroscopy.

The dielectric loss values, ϵ'' , of a semicrystalline PEEK sample are presented as a function of frequency for several temperatures in fig. 2a. The thermal history of the semicrystalline sample was the same as that described in section 3.1 (trace (a) in fig. 1). In the investigated temperature range ($T > T_g$) the α relaxation appears as a maximum in ϵ'' which is accompanied by a strong increase of ϵ'' at lower frequencies. The frequency of maximum loss F_{max} shifts towards higher values as temperature increases. For the sake of comparison, dielectric loss values of an amorphous PEEK sample are presented in fig. 2b. In this case the values of ϵ'' are higher than the obtained ones for the semicrystalline sample. The relaxation peak is centered around 10^4 Hz at $T=433$ K for

the amorphous sample, and at 453K for the semicrystalline sample. This indicates that a displacement of the α relaxation towards higher temperatures takes place when the sample is semicrystalline. It is to be noted that while the intensity of the relaxation peak decreases with increasing temperature for the amorphous sample, the opposite trend is found for the semicrystalline one.

The α relaxation is attributed to segmental motions of the polymer chains appearing at temperatures higher than T_g . The strong increase of ϵ'' at low frequencies is due to the contribution of the electrical conductivity. At each temperature, ϵ'' values for both the semicrystalline and amorphous samples were fitted according to eq. 1 and the result of this treatment is presented in fig. 2 by the continuous lines. The separate contribution of both, the relaxation and the conduction processes is represented. From the analysis of the experimental dielectric curves the characteristic parameters of eq. 1 such as $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$, b , c , τ_0 , σ and s are obtained. Table I and II summarize these values for the experimental results of fig. 2.

In fig. 3, the F_{max} values for the semicrystalline sample are represented as a function of the reciprocal temperature. The dependence of F_{max} with temperature clearly exhibits a non-Arrhenius behaviour. A Vogel-Fulcher-Tamann (VFT) function of the type:

$$F_{max} = F_0 \exp\left[\frac{-A}{T - T_0}\right] \quad (4)$$

can satisfactorily describe the experimental results with the following parameters: $A=648.7$ K, $T_0=410$ K and $F_0=2.7 \cdot 10^{10}$ Hz.

3.3 Incoherent Quasielastic Neutron Scattering.

Incoherent Quasielastic Neutron Scattering (IQNS) experiments were performed at selected temperatures in the range from 300 K to 650 K. Fig. 4 shows IQNS spectra for the highest measured Q ($1.95 \text{ \AA}^{-1}$) at different temperatures. The experimental data are represented by circles. For temperatures below 450K no quasielastic broadening can be detected and the quasielastic scattered intensity falls into the experimental resolution of the spectrometer. At these temperatures the experimental data can be fitted simply by a $\delta(\omega)$ -function. As temperature increases the quasielastic component appears. In the temperature range 500K-600K the data can be fitted to a model function consisting of a sum of a $\delta(\omega)$ and a lorentzian function (eq. 3). The continuous curves represent the best fit according to this model function where the separated contribution of both, the δ -functions and the lorentzian curves convoluted with the experimental resolution, are presented. The Q -structure of this quasielastic broadening is shown in fig. 5 where IQNS spectra are represented at a fixed

temperature ($T=550\text{K}$) for different Q -values. An increase of the quasielastic broadening and a decrease of the height with the Q -vector is observed.

From the analysis of each quasielastic spectrum according to eq. 3 two functions can be extracted: (a) the Elastic Incoherent Scattering Function (EISF), defined by $A_0(Q)$ in eq. 3 and (b) the Half Width at Half Maximum of the lorentzian function ($\Gamma(Q)$). Figs. 6a and 6b show $A_0(Q)$ and $\Gamma(Q)$ as a function of Q obtained for the four spectra at temperatures above 450K. As one can see, A_0 values initially decrease with increasing Q and finally tend to constant values. In the molten state, $T=650\text{K}$, only the low Q spectra present a small evidence of elastic component while for $Q > 0.5\text{\AA}^{-1}$ $A_0(Q) = 0$. Fig. 6b shows $\Gamma(Q)$ as a function of Q for the measured temperatures. For the highest measured temperatures, in the molten state, a large part of the signal is no longer within the observation window and $\Gamma(Q)$ is only accessible for $Q < 0.5\text{\AA}^{-1}$.

4 Discussion

4.1 IQNS: Jump diffusion within a restricted volume

IQNS measurements (fig. 4 and 5) indicate the existence of a molecular motion with an elastic and a quasielastic contribution. The existence of an elastic component, provided by the EISF values shown in fig. 6a, is both, temperature and Q -dependent. This is characteristic of a motion taking place within a

restricted geometry [24, 27, 28, 29]. In this case, the EISF, $A_0(Q)$, is the Fourier transform of the restricted volume [24, 25] while the Q -dependence of $A_0(Q)$ contains the geometrical parameters of the volume.

It is well known in polymers the existence of entanglements that restrict the free motion of a polymer chain [30]. Due to this, polymer chains exhibit a certain degree of confinement imposed by the presence of the neighbor chains. Quasielastic neutron scattering experiments have provided evidence of this restricted dynamics and about the size of the confinement range [31]. In another approach, it has been proposed that relaxation in glass forming liquids takes place in cooperatively rearranging regions (CRR) [32, 33]. The size of these domains diverges as T_g is approached from higher temperatures [32]. Experimental techniques including dielectric spectroscopy [34], calorimetry [33], light scattering [35] and X-ray scattering [36] have shown that the size of these domains may range from 7 Å to about 22 Å at T_g depending on the system. According to that, the validity of the jump diffusion model in a restricted volume to describe our experiments is not surprising if one considers that the volume which can be explored by the proton is strongly restricted by two reasons. Firstly, the above commented interaction with neighboring chains that restricts the available space and secondly, the presence of crystals which restrict the availability of spacial conformations.

Usually, the EISF depends on geometrical factors but not on temperature [24]. However, in our case EISF exhibit a clear temperature dependence (fig. 6a). A temperature dependence of the EISF has been observed in polymeric samples with certain level of order [29, 37] suggesting the existence of protons with different dynamics in the sample. NMR experiments also may provide evidence about the existence of different levels of mobility in the amorphous phase of semicrystalline polymers [6, 7, 8] including PEEK [38]. The simplest possibility to account for this finding within the model is to consider two kinds of proton scatterers. A fraction $n(T)$ contributing to a jump diffusion motion in a restricted volume and the rest, $1-n(T)$, remaining immobile. The fraction of immobile protons must be understood as those protons with mobility well below the lower limit of the dynamic range of the spectrometer. Hence, eq. 3 could be rewritten as:

$$S_{inc}(Q, \omega) = n(T)\{A_0(Q) \cdot \delta(\omega) + [1 - A_0(Q)]L(\omega, \Gamma(Q))\} + [1 - n(T)] \cdot \delta(\omega) \quad (5)$$

The observed EISF could then be described by the function:

$$F_{EISF}(T, Q) = n(T)[A_0(Q) - 1] + 1 \quad (6)$$

The simplest case of diffusion within a restricted region is the one-dimensional diffusion of a particle between two rigid and impermeable boundaries. Consid-

ering that the two boundaries are separated by a distance L the elastic structure factor is given by [27]:

$$A_0(Q) = j_0^2(QL/2) \quad (7)$$

where j_0 is the spherical Bessel function of first kind and zero order. A fit of the experimental F_{EISF} values to eqs. 6 and 7 is presented in fig. 6a by the dotted lines. For 630 K and 650 K , in the molten state, F_{EISF} values tend to zero as Q increases according to eq. 7. This indicates that all the proton scatterers are in motion i.e. eq. 6 is strictly valid with $n(T)=1$. From the fittings of F_{EISF} to the experimental results, the values for L and $n(T)$ have been extracted (see table III). Fig. 7a and 7b present these values as a function of temperature. As one can see, both magnitudes, $n(T)$ and L , nearly increase linearly with temperature until the melting temperature. The rise of $n(T)$ with temperature indicates a progressive mobilization of initially immobilized protons. The separation in mobile and immobile protons is just a first approximation to the problem. Physically, there should be a distribution of temperature activated mobilities. In this context the increment of $n(T)$ can be interpreted as an increase of the number of mobile units with $\tau \approx 10^{-9}$ s. In the molten state no variation of the number of proton scatterers with temperature is observed because all the protons are expected to be in motion and therefore

$n(T)=1$. Since the temperature range covered by us is $212 \text{ K} > (T-T_g) > 32 \text{ K}$ then the absolute values of $5 \text{ \AA} < L < 10 \text{ \AA}$ are within the considerations of the CRR scheme.

The experimental values of $\Gamma(Q)$ (fig. 6b) show an asymptotic behaviour at high Q -vectors. This finding indicates that this motion is not a simple continuous diffusion because, in this case, a $\Gamma(Q) = D_{diff} \cdot Q^2$ behaviour, where D_{diff} is the diffusion constant, should be expected [25]. An asymptotic behaviour at large Q , for $\Gamma(Q)$ can be obtained by considering that diffusion takes place by a means of a jumping mechanism between different sites [27]. In this model the characteristic parameters are the jump length, r_0 and the residence time τ . If one considers a gaussian distribution of jump lengths, , the experimental data of fig. 6b can be analyzed by using the following expression [27]:

$$\Gamma(Q) = \frac{1}{\tau} [1 - \exp(-\frac{Q^2 r_0^2}{2})] \quad (8)$$

In fig. 6b the fitting of this equation with the experimental values is shown by the dotted curves. From this fitting a value for the characteristic jump parameter $r_0 \approx 2.5 \pm 0.4 \text{ \AA}$ is obtained. The corresponding values for the residence time τ (see tab III) have been represented in fig. 3 as a function of the reciprocal temperature.

It is noteworthy that the previous analysis of EISF assumes that the motion

takes place in a restricted volume with a characteristic parameter $L(T)$. However, the model for $\Gamma(Q)$ described in eq. 8 predicts that $\Gamma(0)=0$ for $Q=0$ which is characteristic of a motion occurring within an infinite volume. The existence of a restricted volume modifies the $\Gamma(Q)$ behaviour at low Q , especially in the range between 0 and $2\pi/L$ [27]. Volino and co-workers [28] studied a continuous diffusion in a restricted volume of given geometrical shapes. Hall and Ross [27] calculated the one-dimensional case of the spatially bounded random jump in a volume limited by two boundaries assuming a Gaussian distribution of jump lengths. The asymptotic value ($Q \rightarrow 0$) for both models is the same. The model found for $S_{inc}(Q, \omega)$ follows:

$$S_{inc}(Q, \omega) = A_0(QL) \cdot \delta(\omega) + \sum_{n=1}^{\infty} A_n(QL) \cdot L(\omega, \Gamma_n(QL)) \quad (9)$$

This equation consists on an elastic component; a $\delta(\omega)$ function with an amplitude $A_0(QL)$ (eq 7), and a quasielastic component; an infinite series of lorentzians $L(\omega, \Gamma_n(QL))$ each one with amplitude $A_n(QL)$ given by:

$$A_n(QL) = \frac{(2QL)^2}{[(QL)^2 - (n\pi)^2]^2} [1 - (-1)^n \cos(QL)] \quad (10)$$

The HWHM, $\Gamma(QL)$, of the lorentzian functions $L(\omega, \Gamma_n)$ is expressed by:

$$\Gamma_n(QL) = \frac{1}{\tau} [1 - \exp(\frac{-n^2 \pi^2 r_0^2}{2L^2})] \quad (11)$$

where again r_0^2 is the mean-square jump length and τ is the residence time between two successive jumps. In this model the width of each Lorentzian function is independent of Q . The Q -dependence of the infinite sum of eq. 9 comes from the amplitudes A_n .

The parameters of this model are τ , L and r_0 . Taking for these parameters the values of tab.III we calculated $S_{inc}(Q, \omega)$ according to eq 9. Forty terms of the series were taking into account. The resulting quasielastic contribution can be fitted to a single Lorentzian with a Q dependent width which it is considered as the HWHM. Considering that A_n decreases as $1/n^4$ for fixed QL [27] then the series converges rapidly. Calculations considering more terms do not modify the HWHM values.

The resulting HWHM values as a function of Q calculated at three temperatures for the semicrystalline sample are drawn in fig. 6 as continuous curves. As seen, the model describes the trend of the experimental data within the error of measurement. Moreover, at low Q -values the large range characteristics of the motion are observed. Therefore, the effect of the boundaries is reflected in the experiments by $\Gamma(Q) \neq 0$. Indeed, by comparing $\Gamma(Q)$ obtained either from the jump diffusion in an infinite volume model (dotted line in fig. 6 or from the jump diffusion in a restricted volume model (continuous line in fig. 6) one observes that the stronger differences appear in the low Q region for $Q \ll 2\pi/L$

. The limited Q-range prevent us for giving a more accurate description in the low-Q region.

4.2 Molecular origin of the quasielastic broadening.

The obtained values for both r_0 and L can be interpreted considering that the proton-proton distance in the phenyl ring is about $4.3\text{\AA}$. Thus the calculated L values are in agreement with a motion of the proton in an effective space larger than that defined by a flip of the phenyl ring. Here, the elementary jumps, characterized by r_0 , can be associated to a motion of the proton around its covalent bond. The L variation with temperature (fig. 7b) indicates that the motion is not just a simple flip or rotation of the benzene ring but also involves a certain degree of translation. In support of this, it is to be noted that localized benzene motions are typically faster than those investigated by the IN10 spectrometer and frequently appear in the meV energy range [12, 39]. Moreover, by comparing the loss of elastic intensity with temperature with the first appearance of quasielastic broadening, it seems that there must be a quasielastic contribution, probably from a localized motion, at a higher frequency scale, i.e. higher energy range than that covered by us [40]. Hence, we can attribute the quasielastic broadening appearing in the measured temperature and Q range to the α relaxation process. Dielectric spectroscopy measurements reveal the existence of

a molecular motion in the investigated temperature range which is attributed to the segmental motions giving rise to the α relaxation (fig. 2) [10, 19]. Due to the broad frequency band used in the dielectric spectroscopy experiments, F_{max} values can be directly compared with the corresponding ones derived from the IQNS experiments considering that $F_{IQNS} = 1/(2\pi\tau)$. In fig. 3 both F_{max} from the dielectric experiments and F_{IQNS} values are represented.

A VFT behaviour is observed for the F_{max} values as expected for the α relaxation process. The absolute values of F_{max} and F_{IQNS} differ by about one order of magnitude at 500K and tend to merge together at higher temperatures approaching the calculated VFT curve. The differences of the absolute values as measured by the two different techniques can be attributed to the different molecular probes used in both techniques. The molecular probe in the dielectric experiments is the dipole moment of the ketone, ether and benzene groups while in the IQNS experiments are the protons attached to the phenyl rings. Consequently, IQNS experiments reveal the contribution of the phenyl rings to the α relaxation while dielectric experiments shows up the overall segmental motion. The good overlap of IQNS and DS in fig. 3 suggest, that the same relaxation process is being observed by both techniques.

4.3 Influence of crystallinity on the dynamics

Dielectric experiments performed in, both, amorphous and semicrystalline PEEK above T_g reveal a temperature dependence of τ corresponding to the α relaxation strongly deviated from an Arrhenius behaviour. The strong-fragile scheme proposed by Angell, allows one to classify glass forming liquids on the basis of the temperature dependence exhibited by the corresponding relaxation times (τ). By scaling τ -values as a function of T_g/T , the relaxation time temperature dependences of systems with different T_g values can be compared. Within this scheme, the fragility of a system is defined as the degree of departure from the Arrhenius behaviour exhibited by the relaxation time of the α relaxation process [41]. The parameter A from the VFT equation (eq. 4) can be replaced by $D \cdot T_0$ where D is called here the strength parameter [41]. In polymers, fragility has been associated with the strength of the correlation between non bonded species and has been renamed cooperativity [42].

In fig. 8 we have replotted the F_{max} data of fig. 3 as a cooperativity plot (τ vs. T_g/T). The dielectric relaxation time, τ , has been calculated according to $\tau = 1/(2 \cdot \pi F_{max})$. For the sake of comparison, PEEK dielectric data taken from the literature [10] have been included. The characteristic τ calculated by IQNS experiments were taken from table III. Data for amorphous and semicrystalline PEEK were normalized to the calorimetric T_g value (fig. 1). Although

semicrystalline and amorphous samples exhibit different T_g values, upon scaling by T_g/T , τ -values tend to collapse into a single curve, in agreement with previous experiments and theoretical predictions[42].

It is evident that the α relaxation times for PEEK strongly deviate from an Arrhenius behaviour which would correspond to a straight line in this plot. This effect is quantified by a small value of the strength parameter ($D=1.5$). This value is smaller than the reported values for other polymers including benzene rings in the backbone like poly(ethylene terephthalate) (PET) and polycarbonate from bisphenol A (BPA-PC) [41, 43]. This could be attributed to the higher rigidity of the chain structure of PEEK as compared with PET and BPA-PC. It is noteworthy that the least fragile polymer reported exhibits a value of $D=16$ (polyisobutylene) [44].

Owing to the existence of crystallinity, in the semicrystalline sample the α relaxation appears as a symmetric ($c=1$) and relatively broad process (low b values, tab.I). In contrast to what happens in amorphous PEEK, the dielectric strength, $\Delta\epsilon$, for the semicrystalline sample increases with temperature (tab.I, fig. 7a). This effect has been previously reported for semicrystalline PEEK samples [10, 19]. According to the Kirkwood-Fröhlich equation [3], in a first approximation, the dielectric strength is directly proportional to the amount of dipoles involved in the relaxation and inversely proportional to the temperature

as:

$$\Delta\epsilon \propto \frac{N}{T}g(T)\mu^2(T) \quad (12)$$

where N is the number of dipoles, μ is the effective dipole moment and g is the correlation factor which contains contributions of both, inter and intra-chain dipolar correlation. The $\Delta\epsilon$ increase with temperature can be attributed to a progressive mobilization of dipoles involved in the relaxation giving rise to a temperature dependence of N [10, 19]. In semicrystalline polymers, the dipoles included in the crystals are at fixed positions and cannot contribute to the α relaxation process. It has been proposed that a given part of the dipoles are included in a rigid amorphous phase (RAP) whose mobility increases with temperature [10, 19]. This means that the material belonging to the RAP does not contribute to the overall crystallinity because it is in an disordered region though it can relax depending on temperature [10]. In our case, evidence about the existence of the RAP has been given not only by the DSC experiments (fig. 1), which at T_g gives for the RAP a value of 0.18, but also from the IQNS experiments. Since that the crystallinity of PEEK in our experiments is $X_c \approx 0.34$ one observes that the fraction of immobile material derived from IQNS experiments, $1-n(T)$, is also higher than that expected on the only basis of the crystalline material. Moreover, our present results confirm

the existence of a RAP when comparing the measured $\Delta\epsilon$ values, in our case, with the amount of mobile protons, $n(T)$, as derived by IQNS experiments (fig. 7). Both magnitudes increase with temperature in a similar manner. As both magnitudes, $\Delta\epsilon$ and n , give information about the amount of mobile material the progressive incorporation of a fraction of initially immobile material to the relaxation process, as temperature increases, seems to be confirmed by two different techniques.

A final remark has to be made about the physical meaning of the restricted volume in our case. Results presented in fig. 7 indicate that L increases with temperature up to the melting point and then remains constant. By comparing L values for the semicrystalline and the molten sample (Fig. 7b) the restrictions in the dynamics imposed by the crystals appears as a decrease in the size of L . The fact that, the L values are much smaller than the size of the calculated amorphous layer ($\approx 125 \text{ \AA}$) [15] and, that, L decreases with decreasing temperature, favours the existence of a rigid amorphous phase whose mobility increases with temperature. Further experiments extended to a higher dynamic and temperature range are necessary to shed light on this point.

5 Conclusions

By combining dielectric spectroscopy (DS) and incoherent quasielastic neutron scattering (IQNS) the molecular dynamics of semicrystalline poly(ether-ether-ketone) (PEEK) could be studied in the glassy, semicrystalline and molten state. It is shown that the origin of the quasielastic broadening observed in the IQNS spectra for $T > 450$ K is the α relaxation process which manifests itself as a maximum in the imaginary part of the complex dielectric permittivity (ϵ''). The motion observed by IQNS experiment has been described as a jump diffusion process taking place within a restricted volume whose size gradually varies with temperature from $L=5\text{\AA}$ up to $L=8\text{\AA}$ in the semicrystalline sample, and discontinuously increases to $10\text{\AA}$ near the melting point. The analysis of the IQNS spectra indicates: i) that the amount of mobile protons is smaller than the calculated on the exclusive basis of the DSC crystallinity and ii) that their amount rises with temperature. Similarly, the amount of mobile dipoles estimated from $\Delta\epsilon$ for the semicrystalline specimen shows up an increase with temperature. The above effects support the existence, in semicrystalline polymers, of a confined amorphous phase with regions of different degree of mobility.

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Table I. $\Delta\epsilon$, b , τ_0 , σ and s values obtained from the fitting of equation 1 in the case of the α relaxation of the semicrystalline sample.

T(° C)	$\Delta\epsilon$	b	$\tau_0(s)$	σ	s
443	0.53	0.33	$2.2 \cdot 10^{-4}$	$5.8 \cdot 10^{-12}$	0.59
453	0.53	0.38	$7.4 \cdot 10^{-6}$	$2.7 \cdot 10^{-11}$	0.62
473	0.57	0.36	$1.1 \cdot 10^{-7}$	$3.6 \cdot 10^{-10}$	0.72
483	0.61	0.39	$2.5 \cdot 10^{-8}$	$9.0 \cdot 10^{-11}$	0.73
493	0.62	0.41	$7.5 \cdot 10^{-9}$	$1.5 \cdot 10^{-9}$	0.73

Table II. $\Delta\epsilon$, b , c , τ_0 , σ and s values obtained from the fitting of equation 1 in the case of the α relaxation of the amorphous sample.

T(° C)	$\Delta\epsilon$	b	c	$\tau_0(s)$	σ	s
423	1.50	0.78	0.46	$1.9 \cdot 10^{-2}$	$6.7 \cdot 10^{-13}$	0.99
428	1.42	0.82	0.44	$8.7 \cdot 10^{-4}$	$2.31 \cdot 10^{-12}$	0.90
433	1.29	0.72	0.53	$7.1 \cdot 10^{-5}$	$2.35 \cdot 10^{-12}$	0.56

Table III. r_0 , τ , L , and n values obtained from the analysis of the EISF and the HWHM ($\Gamma(Q)$).

T(K)	$r_0(\text{\AA})$	$\tau(s)$	$L(\text{\AA})$	n
500	2.4	$1.4 \cdot 10^{-9}$	5.1	0.3
550	2.4	$5.3 \cdot 10^{-10}$	6.4	0.4
600	2.9	$3.6 \cdot 10^{-10}$	8.0	0.5
650	-	-	10	1

Legends to the figures.

Figure 1: DSC scans of initially semicrystalline (a) and amorphous (b) PEEK.

Heating rate: 20K/min

Figure 2: Dielectric loss values, ϵ'' , for semicrystalline (a) and amorphous (b) PEEK. Different symbols represents the three different spectrometers used (see experimental section). Lines represent best fits according to eq. 1. Thinner lines represent the separate contribution of the conduction and relaxation processes.

Figure 3: Frequency of maximum loss, F_{max} , values as a function of reciprocal temperature (open symbols). Different symbols represent data obtained by using different spectrometer. Full symbols represent the equivalent frequency ($F = 1/(2 \cdot \pi \tau)$) obtained from the IQNS data. Continuous line represents the best fit of the experimental data to the VFT equation.

Figure 4: Quasielastic neutron scattering spectra as a function of temperature for $Q=1.95 \text{ \AA}^{-1}$ value. Experimental points (o), (-) experimental resolution, lorentzian curve and best fit according to eq.3.

Figure 5: Quasielastic neutron scattering spectra for four selected Q -values at $T= 550\text{K}$. Same symbols as in fig.4

Figure 6: (a) Elastic incoherent scattering factor, EISF, and (b) $\Gamma(Q)$ as a function of Q at different temperatures: $\circ$ 500 K, $\bullet$ 550 K, $\square$ 600 K, $\blacksquare$ 630 K, $\triangle$ 650 K. Dotted lines represent the best fit of the experimental points to a jump diffusion model. Continuous lines in (b) correspond to a jump diffusion model in a restricted volume. Dashed line is a guide for the eye.

Figure 7: (a) Temperature dependence of $\Delta\epsilon$ calculated from dielectric spectroscopy for the amorphous ($\bullet$) and semicrystalline sample ($\circ$) and $n(T)$ calculated from IQNS experiments ($\square$). (b) L , characteristic length of the restricted volume calculated from IQNS experiments.

Figure 8: Cooperativity plot: τ versus T_g/T for PEEK. T_g is the calorimetric glass transition. Full symbols corresponds to amorphous PEEK and empty symbols to semicrystalline PEEK: $\triangle$ from ref.10 , and $\circ$ from this work, $\oplus$ IQNS data. The dotted lines correspond to several strength parameters D values. The continuous line represent the best fit to the data according to the VFT equation.

Fig.1

Fig.2

Fig.3

Fig. 4

Fig. 5

Fig. 6

Fig.7

Fig. 8