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Induction time for cold crystallization in semi-rigid polymers: PEN and PEEK

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Abstract

The appearance of long range density fluctuations in two isotropic semi-rigid polymers (PEN and PEEK), during the induction period prior to crystallization, when heating above the glass transition temperature, T_g, has been demonstrated by simultaneous wide- and small-angle X-ray scattering techniques. The parallel use of dielectric spectroscopy, to characterize the segmental dynamics of the amorphous polymers polymer above T_g, and of X-ray scattering, to estimate the induction period for cold crystallization, reveals that segmental mobility of the supercooled melt is a key factor in controlling the development of the pre-crystalline nanostructures. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Semi-rigid polymers; Cold crystallization; X-ray scattering

1. Introduction

Quenching of a crystallizable polymer melt within the window between the thermodynamic melting point(T_m^0) and a temperature above the glass transition temperature (T_g) may induce a partial ordering of the supercooled melt into nanometer-scale crystals embedded within a matrix of uncrystallized amorphous material [1–3]. In isotropic polymers, crystallization usually proceeds through nucleation-and-growth mechanism [3] leading to the formation of a micrometer-scale organization of crystalline lamellae arranged within spherulites, axialites or other supramolecular structures [1–3]. However, nucleation-and-growth is not the only mechanism inducing the development of a two-phase system consisting of amorphous and crystalline regions. Oriented amorphous polymers, may exhibit crystallization processes governed by the spinodal decomposition (SD) mechanism [3]. Owing to the fact that the formation of a stable crystallite implies the appearance of surfaces, the nucleation step requires an induction time, t_i, where no crystals are present. While polymer crystallization for $t > t_i$ has been both theoretically [4,5] and experimentally [6] extensively described, the use of time-resolved techniques has only recently provided experimental access to structural phenomena occurring at $t < t_i$ [7–9]. In particular, simultaneous wide- and small-angle X-ray scattering (WAXS and SAXS, respectively) experiments [8–12] performed on isotropic melts during the induction time of crystallization reveal the existence of an excess of scattering at low angles. These experiments include the study of rigid polymers [11], semi-rigid polymers [8,13,14], flexible polymers [9,10,15], and low molecular weight systems [16]. Although, the latter has been interpreted by some authors as a signature of precrystalline ordering phenomena of spinodal nature [8,13,17], alternative explanations, for flexible polymers, have been also proposed [12,15].

Regardless of the crystallization scenario invoked, one may expect a significant influence of the segmental mobility of the supercooled melt on the development of any precrystallizing textures especially for cold crystallization where the system is heated up from the glassy state. The presence of frictional forces appearing among neighbouring chain segments should affect any kind of material reorganization. Although thorough attempts have been made in this direction [18], the relation between segmental mobility and structure formation is not fully understood, especially as regards the influence of molecular dynamics of the amorphous phase on the structure development during the induction time preceding crystallization.

In this paper we report dielectric and WAXS–SAXS experiments for two selected semi-rigid polymers having different T_g values. The aim of the present study is to establish a possible

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relationship between segmental mobility and nanostructure development during the precrystallization process.

2. Experimental

As model polymers we have chosen poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) (Eastman) and poly(aryl ether ketone ketone) (PEEK) (ICI), having T_g values of 393 and 418 K, respectively. In both cases, amorphous films were obtained by quenching the polymers from the molten state as reported elsewhere [19]. Simultaneous WAXS and SAXS measurements were performed using a double-focusing mirror monochromator camera on the polymer beam line A1 at HASYLAB (Hamburg, Germany). Cold crystallization was carried out isothermally bringing the sample up to the crystallization temperature at a constant heating rate of 10 K/min from the glassy state. Scattering patterns were recorded by using two linear position-sensitive detectors. Corrections for fluctuations in the intensity of the primary beam and background were carried out [20]. The data acquisition system is based on CAMAC hardware and modulator software [21]. Measurements of the complex dielectric permittivity, $\epsilon^* = \epsilon' - i\epsilon''$, were performed in the amorphous polymers over a frequency window of 10^{-1} Hz $< F < 10^5$ Hz, in a temperature range of $123\ \mathrm{K} < T < 423\ \mathrm{K}$ using a Novocontrol system integrating a SR 830 lock-in amplifier, a dielectric interface and a QUATRO temperature control system. A detailed description of the measurement protocol and data treatment procedure has been published elsewhere [22].

3. Results

3.1. Simultaneous WAXS–SAXS experiments

Figs. 1 and 2 illustrate the variation of the WAXS and SAXS patterns as a function of the reciprocal lattice vector, $q = (4\pi/\lambda)\sin\theta$, for different time in two selected isothermal crystallization experiments performed with PEN and PEEK. The scattering patterns were obtained with an accumulation time of 1 min. The SAXS intensities were multiplied by a factor q^2 in order to accomplish the Lorentz correction [23]. Fig. 1 shows the scattering data for PEN

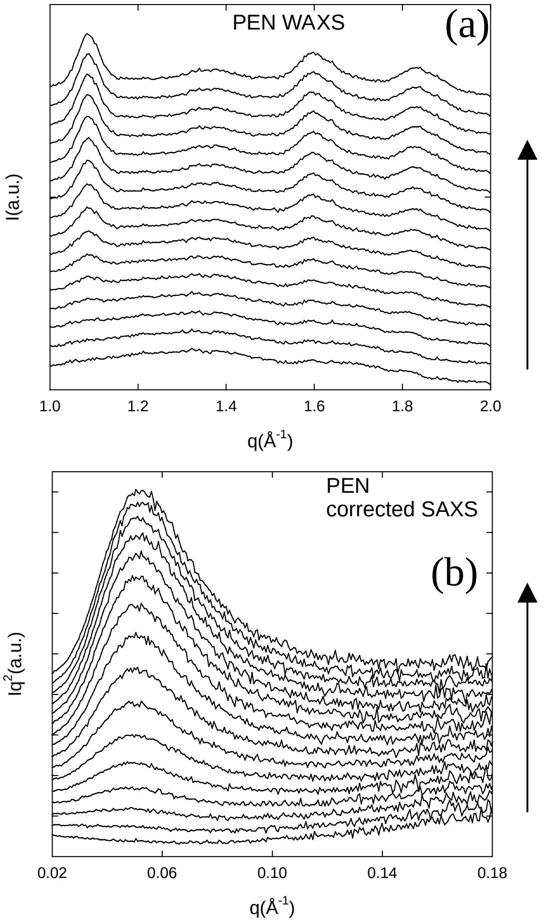

Fig. 1. Simultaneous (a) WAXS and (b) SAXS experiment during crystallization of initially amorphous PEN at $T_c = 438$ K. Crystallization time, t_c increases in the direction of the arrow. Time from top to bottom (in minutes): 0, 4, 8, 12, 16, 20, 24, 28, 32, 36, 40, 44, 48, 52, 56, 60.

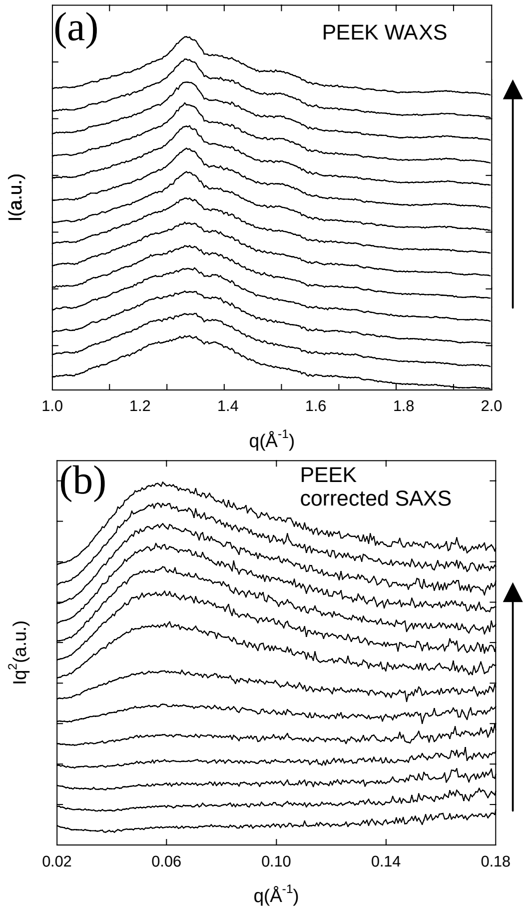

Fig. 2. Simultaneous (a) WAXS and (b) SAXS experiment during crystallization of initially amorphous PEEK at $T_c = 428$ K. Crystallization time, t_c increases in the direction of the arrow. Time from top to bottom (in minutes): 0, 4, 8, 12, 16, 20, 24, 32, 40, 48, 56, 64, 72, 80.

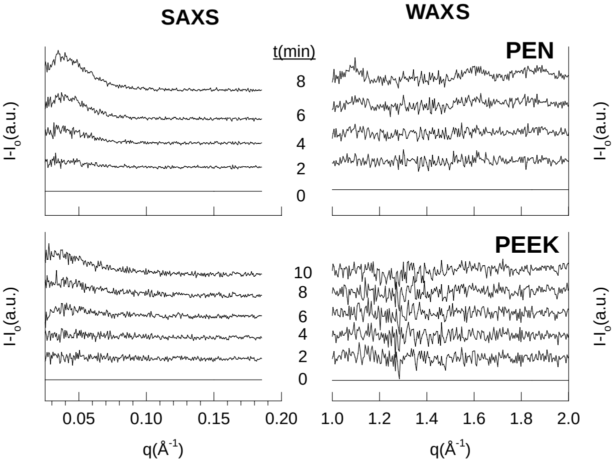

Fig. 3. Simultaneous $I - I_0$ WAXS and SAXS intensities for early stages of isothermal crystallization of the initially amorphous polymer system: upper, PEN; lower, PEEK. Crystallization time in minutes is labelled in every curve.

taken at $T_c = 438$ K. Similarly, Fig. 2 shows the corresponding scattering results for PEEK at $T_c = 428$ K. With an aim to examine in detail the induction time region in both cases, the initial scattering pattern was subtracted from all the others in order to better detect the appearance of the Bragg peaks (appearance of crystalline regions) in the WAXS and of the excess of scattering in the SAXS experiments (Fig. 3). From here, it is possible to estimate values for the induction time for crystallization of $t_i = 5 \pm 1$ min for PEN and of $t_i = 10 \pm 1$ min for PEEK at the corresponding T_c. Most interesting is the appearance in the SAXS experiments of a conspicuous excess of scattering at low angles ($q < 0.05$ Å^{-1}) within the induction period. This behaviour is in agreement with previous findings [8,9,11,13,14] supporting the hypothesis that under certain conditions, long range density fluctuations of semi-rigid polymers are responsible for ordering phenomena occurring during the induction period prior to crystallization. From simultaneous WAXS–SAXS experiments, values for t_i, at different crystallization temperatures were obtained for both polymers. Fig. 4a illustrates the various t_i values obtained as a function of the reciprocal temperature for PEEK and PEN. An induction time of 1500 s measured recently for PEN [14] at $T = 428$ K has been included.

3.2. Dielectric experiments on the amorphous polymers

The dynamics of the two amorphous polymeric systems was characterized by dielectric spectroscopy. Fig. 5 shows the ϵ'' values as a function of frequency, at different temperatures, for PEN (Fig. 5a) and for PEEK (Fig. 5b). The continuous curves are fits of the experimental data to the Havriliak–Negami (HN) equation as discussed elsewhere [22,24]. It is important to emphasize that during these measurements no crystallization takes place. Thus, the experiments characterize the dynamics of the amorphous polymers before crystallization. From these results

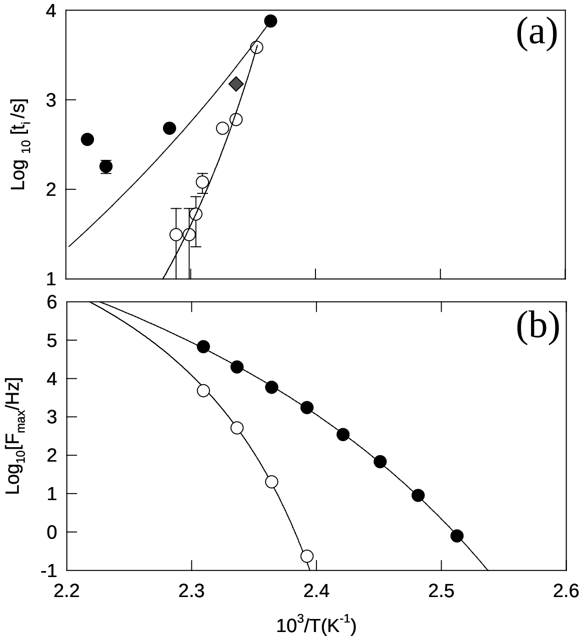

Fig. 4. (a) Logarithm of the induction time, t_i, as a function of the reciprocal temperature for PEN (●) and PEEK (○), (◇) induction time for PEN taken from Ref. [14]. (b) Logarithm of the frequency of maximum loss, F_{max} for PEN (●) and PEEK (○) as a function of the reciprocal temperature. Continuous lines are theoretical fits to the Vogel–Fulcher–Tamann equation. For every polymer, the parameters D and T_0 are the same for t_i and F_{max}.

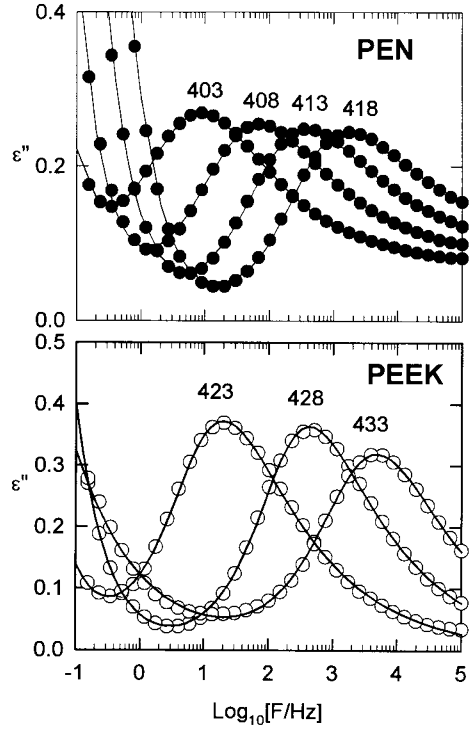

Fig. 5. Dielectric loss values, ϵ'', for PEN and PEEK as a function of frequency for different temperatures labelled in Kelvin. Lines represent best fits according to the Havriliak–Negami equation.

values for the frequency of maximum loss, $F_{\max}$, were obtained as a function of the reciprocal temperature for the two systems investigated (see Fig. 4b). Here the continuous lines are the best fits to the Vogel–Fulcher–Tamann (VFT) equation $F_{\max} = F_0 \exp[-DT_0/(T - T_0)]$, where D is the fragility strength, F_0 is the limiting frequency at high temperatures and T_0 is a reference temperature with $T_0 < T_g$. In the present case the following values were obtained: $F_0^{\mathrm{PEEK}} = 5.0 \times 10^{10}$ Hz; $F_0^{\mathrm{PEN}} = 9.8 \times 10^{13}$ Hz; $D^{\mathrm{PEEK}} = 1.55$; $D^{\mathrm{PEN}} = 5.6$; $T_0^{\mathrm{PEEK}} = 394.9$ K *and* $T_0^{\mathrm{PEN}} = 340.2$ K. It is noteworthy that by considering the D and T_0 values derived from the dielectric (dynamic) measurements, a good description of t_i, as derived from the X-ray structural measurements, is obtained for PEEK and PEN. In the former a good fit between dielectric and X-ray data is obtained in the whole measured range and for the later at low temperatures considering $t_i \propto \exp[DT_0/(T - T_0)]$ (continuous lines in Fig. 4a).

4. Discussion

In a classical nucleation and growth process the driving force for crystallization is provided by the chemical potential difference Δg_m between the chemical potentials of a monomer in the amorphous and crystalline phases, respectively [3]. It is known that Δg_m increases with the supercooling, $\Delta T = T_m^0 - T$ [3]. Due to the fact that the formation of a nucleus implies the appearance of surfaces and assuming that $\Delta g_m \propto \Delta T$, the nucleation step occurs at a nucleation rate, ν_{nuc}, given by [3]

$$\nu_{\mathrm{nuc}} \propto \exp(-E/kT) \propto \exp(-C/[T(\Delta T)^2]) \qquad (1)$$

where E is the activation energy for nucleation and C is a constant. As a first approach, one may consider the induction time as the time required for the first stable nucleus to appear. Therefore

$$t_i^{\mathrm{nuc}} \propto \exp(C/[T(\Delta T)^2]) \qquad (2)$$

For spinodal assisted nucleation in homopolymers, a phenomenological theory has been developed in which it is shown that the coupling between density and chain conformation may induced a liquid-liquid bimodal within the equilibrium liquid-crystalline solid coexistence region [17]. According to this model the induction time is given by

$$t_i^{\mathrm{SD}} \propto t_s + C \exp(\Delta(T, \rho)/kT) \qquad (3)$$

where C is a constant, t_s is a time in which the system reaches a certain spinodal texture consisting of two liquid phases characterized by two different chain conformations, and $\Delta(T, \rho)$ is the activation energy for crystallization corresponding to the liquid phase whose density (ρ) and chain conformation are closer to that of the crystal (ρ_c). This expression can be considered as composed of a kinetic term, t_s, and a thermodynamic term similar to t_i^{nuc} exchanging E by $\Delta(T, \rho)$. Thus, in a first approach one may expect a similar dependence on supercooling as that followed by t_i^{nuc}. Accordingly, the thermodynamic terms would indicate a rapid increase of the induction time as temperature increases. The results obtained in the present work for cold crystallization of PEEK and PEN indicate a decrease of t_i as the temperature increases (Fig. 4a). The good description obtained for the temperature dependence of t_i by using the VFT equation derived from dielectric measurements seems to be an indication of the kinetic nature of the experimental t_i under the investigated crystallization conditions. Consequently, one may attempt to identify t_i with t_s. Moreover, the observed deviation of the t_i values of PEN at the higher investigated temperatures (Fig. 4a) can be interpreted as due to the increasing important role of the thermodynamic term as temperature increases tending to slow down the crystallization process. Indeed, for PEN, a plateau of the crystallization rate has been reported to occur for temperatures in the range $448\ \mathrm{K} < T < 513$ K [25].

5. Conclusions

In summary, for polymers like PEN and PEEK, which can be considered as model systems of semi-rigid systems, it is demonstrated that: (i) during the induction period for crystallization a development of long range nanostructures as revealed by the excess of scattering appearing at low scattering angles occurs; (ii) our measurements reveal a direct correlation of the dynamic measurements (dielectric spectroscopy) with the X-ray structural results indicating that the segmental mobility of the supercooled melt is one of the major factors which controls the development of the precrystalline nanostructure during cold crystallization.

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