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Tie molecules, morphology and confinement effects in semi - crystalline poly(ethylene naphthalene-2,6dicarboxylate) (PEN)

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Abstract. The glass transition dynamics and confinement effects in poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) were studied by broadband dielectric relaxation spectroscopy (DRS) in relation with semi-crystalline morphology. PEN samples were obtained by cold crystallization at different crystallization temperatures (T_c ranging from 165 to 240°C) and crystallization times (t_c from 30min to 24h). Differential scanning calorimetry and X-ray diffraction showed that the crystallinity ratio (X_c) increases when T_c and t_c increase. The glass transition relaxation is shifted to higher temperatures as t_c increases but this confinement effect decreased with increasing T_c . The origin of this anomalous dynamics can be related to (i) the crystalline lamellar stack morphology revealed by small angle X-ray scattering (SAXS) and (ii) chain scission occurring during annealing at the crystallization temperature. As a result, the density of tie-chain molecules (chain portions bridging crystallites) can be considered as the key factor for the understanding of confinement effects in semicrystalline polymers. Accordingly the confinement effects on the glass transition dynamics can be optimally rationalized as a function of a characteristic length intermediate between the interlamellae thickness l_a and that of the theory of Brown and Huang $2l_c+l_a$ where l_c is the crystallite thickness.

1. Introduction

The molecular mobility in semi-crystalline polymers has been studied by several authors using a large number of systems and spectroscopic methods ¹⁻¹⁸. However, there are still few works analyzing simultaneously in details their molecular and nano structure in relation with their dynamics ⁹⁻¹². As a general trend, these studies have commonly revealed an increase in glass transition temperature T_o when the crystallinity ratio is sufficiently high. Obviously, this trend is attributed to the slowing down of the molecular mobility in the amorphous phase that is constrained by the presence of the crystalline

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phase. The confinement effect is due to the participation of the chains within the crystals and can also result in the formation of a rigid amorphous fraction (RAF)^{6,7,19-21}. Cheng and Wunderlich²⁰ previously showed that the glass transition of semi-crystalline PEN increases and an increasing RAF is developed with decreasing crystallization temperatures. Also, in specific crystallization conditions ("constrained" conditions ¹⁸) a different behavior can be observed as a result of a lowering of the density of the amorphous phase. The dynamics of the amorphous phase thus appear to result both from the confinement effects and from the amorphous structural state inherited from crystallization conditions. In addition, confinement was also envisaged to influence the lamellar stacks structuring itself in the crystallization process^{22,23}.

In this context, a general understanding of the relations between thermo-mechanical history, structure and dynamics is still lacking to completely understand the dynamic behavior of these complex systems. In this paper, we have chosen to study the molecular dynamics of Poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) because of the large range of crystallization temperatures that can be assessed to induce crystallization from the amorphous films. PEN is a thermoplastic polyester developed in the 1970s. It combines thermal stability, degradation resistance, good barrier properties and excellent dielectric and mechanical properties⁵. The melting point temperature of PEN ($T_m \approx$ 267°C, measured at a heating rate of 10°C/min) obtained by differential scanning calorimetry (DSC) is about 10°C higher than in the case of PET, while the glass transition temperature ($T_g \approx 120^{\circ}$ C) is about 40°C higher than that for PET ²⁴. The enhanced properties of PEN compared to PET are due to a higher stiffness of the macromolecular chain resulting from the presence of a naphthalene structure (see Scheme 1) ²⁵. Thus, PEN finds a large variety of applications as tire cords for cars²⁶, as electromagnetic tapes (audio, video and computer tapes) ^{27, 28} and in packaging or capacitors industry.



Scheme 1: Chemical structure of poly(ethylene-2,6-naphthalene dicarboxylate)

Several studies on the molecular mobility or the morphology of PEN have already been published^{2,11,12}. However, few of them successfully bridge the gap between dynamics and morphology at the nanoscale. The aim of this work was to illustrate the links between thermal history, semicrystalline morphology and confinement of the amorphous phase by the crystalline lamellae. The arelaxation dynamics is the most affected by crystallinity. Therefore, this paper will deal mainly with the study of a-process in PEN as a function of crystallization conditions. Previous works have shown that α -relaxation of PEN classically shifts to higher temperatures as the result of the confinement of the amorphous phase by the crystalline phase⁴⁻⁷. In addition to the development of the semi-crystalline morphology, a structuration of the amorphous phase is likely to occur with the formation of a rigid amorphous phase, *i.e.* an amorphous contribution that do not contribute to the specific heat increment at the glass transition⁷. Such confinement effects in polymer materials generally lead to a change in the dynamics in the amorphous phase, but slower, faster or unchanged confined dynamics have previously been described²⁹ as a function of the interactions between the rigid confining phase and mobile polymeric phase. This phenomenon is generally probed by the evolution of the calorimetric glass transition or the frequency/temperature location of the α -relaxation process (dielectric, mechanical...etc). A derived issue is the relation between the confinement effects and the details of molecular mobility in terms of intermolecular cooperativity^{30,31}. In this work, the confinement effects

are shown to be mainly governed by the cold crystallization conditions at different temperatures and during different crystallization times.

2. Experimental details

2.1. Materials

Amorphous PEN films with a thickness of 109 μ m were obtained from Du Pont de Nemours with a weight average molecular weight of about 30100 ± 8000 g/mol. Semicrystalline PEN samples were crystallized in situ in the dielectric cell by heating from room to the crystallization temperatures ($T_c = 165$, 180, 220 and 245°C) at a rate close to 10 K/min and subsequent annealing during different crystallization times ($t_c = 0.5$, 2 and 24h). In a second set of experiments, the PEN films were systematically crystallized in an oven at 165, 170, 180, 190, 200, 210, 220, 230, 240 and 245°C during 30 minutes, in order to better follow the influence of the crystallization temperature on the morphology and the resulting molecular mobility. These samples were dried below T_g in the dielectric cell for 2 h at 110°C before the DRS measurements.

2.2. Methods

Broad band dielectric relaxation spectroscopy (BDS) was carried out on the films with circular electrodes having a diameter of 20 mm in parallel plate geometry. A Novocontrol Concept 40 α -analyzer, interfaced to the sample by a Broadband Dielectric Convertor (BDC, Novocontrol), was used to obtain the complex dielectric function:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) \tag{1}$$

where ω is the angular frequency, ε' is the real part, ε'' the imaginary or loss part of the complex permittivity. The measurements were performed in a frequency range from 10^{-1} to 10^{6} Hz and the temperature of the sample varied from -140 to 200° C in isothermal steps every 3 K and was controlled under a nitrogen flow with a stability of $\Delta T = 0.1$ K (Novocontrol Quatro System Controller BDS 1330). The data were analyzed by using the Havriliak-Negami (HN) function to fit them, using the Novocontrol software WinFit. The maximum dielectric loss (ε'') was then determined from the fits of each α -relaxation process to yield a macroscopic relaxation time according to:

$$\tau = 1/2\pi f_{\text{max}} \tag{2}$$

where f_{max} is the frequency at maximum dielectric loss.

DSC measurements were carried out using a 2920 TA Instruments previously calibrated with indium (with a heating rate of 10 K/min). Sample weights were around 5 to 8 mg. The samples were all sealed in aluminum pans and the melting enthalpies were calculated from the areas of the melting peaks using the linear baselines from 160°C to 290°C, as shown in Figure 1. In order to calculate the crystallinity ratio from calorimetry measurements, the melting heat of the fully crystalline state ΔH_f^{∞} was taken equal to 190 J/g³². The values of the glass transition temperatures at the midpoint (T_g) were calculated by using a linear estimation of the baseline before (between 90 and 110°C) and after (between 140 and 160°C) the glass transition.

The semi-crystalline nanostructure of the PEN films was studied by SAXS performed at ESRF (Grenoble France) on BM2-D2AM beam-line. The films were placed perpendicularly to the incident beam. The scattered intensity was corrected from empty cell. Although sophisticated approaches are

possible for the study of the lamellar stack morphology²³, in this work the semicrystalline nanostructure was simply characterized by the scattering vector (q_{max}) of the maximum of the Lorentz-corrected intensity $I(q).q^2$ in order to deduce the long period, L_p from the Bragg equation $L_p=2\pi/q_{max}$, where $q=4\pi\sin\theta/\lambda$ and λ is the incident wavelength. The crystalline lamellae thickness (ℓ_c) and the amorphous thickness (the intercrystalline thickness ℓ_a) were deduced from the mass crystalline ratio X_c deduced from DSC measurements:

$$\ell_c = L_p \cdot X_c / ((\rho_c / \rho_a)(1 - X_c) + X_c)$$
(3)

$$\ell_a = L_p (1 - X_c) / ((\rho_a / \rho_c) X_c + 1 - X_c)$$
(4)

Where $\rho_c=1.407 \text{g/cm}^2$ and $\rho_a=1.325 \text{g/cm}^3$ are the mass densities of the (α) crystalline and amorphous phases respectively³³.

3. Results

3.1. Calorimetry analysis and crystallinity characterization

The thermograms of selected samples crystallized during 24 hours at different crystallization temperatures are reported in Figure 1 in the glass transition range. The large differences observed between the thermograms of samples crystallized at 165°C and 245°C are indicative of different semicrystalline morphologies, associated with different crystalline lamellae thicknesses and/or different crystalline-amorphous interfacial energies and/or different crystalline phases.



Figure 1: DSC thermograms at 10K/min (0.166 K/s) in the glass transition range for the amorphous and the samples crystallized during 24 hours at 165°C, 180°C, 220°C and 245°C.

A decrease of the glass transition temperatures can be observed after crystallization at 245°C, in Figure 1 in agreement with a previous study²⁰. Obviously, these changes in the glass transition dynamics should be related to the differences in the semicrystalline morphology and crystallinity ratios induced by different crystallization conditions. Nevertheless, the glass transition temperatures are difficult to obtain precisely from the thermograms, in particular due to the presence of the secondary endothermic peaks and the low values of the heat capacity increments ΔC_p associated to the

glass transition in semicrystalline systems. More detailed results can be obtained with more sensitive techniques such as BDS.

The effect of crystallinity ratio X_c obtained by DSC can first be discussed in Figure 2, displaying the values of X_c as a function of T_c . Clearly, the decrease in the glass transition temperatures with crystallization temperatures shown in Figure 1 cannot be interpreted as the direct result of the increase of the crystallinity ratio with T_c as observed in Figure 2. The details of the morphology and macromolecular structure must be further analyzed in order to interpret the changes in the dynamics.

Figure 2 (open squares) displays a systematic evolution of crystallinity ratio with crystallization temperature at a constant crystallization time of 30 min. Two crystallization regimes can be distinguished in this figure: at crystallization temperatures below 210°C, the increase of X_c with T_c is limited in the range 0.27-0.29. A stronger increase is observed for the samples crystallized above 210°C, with a limiting crystalline ratio just above 0.34.



Figure 2: Mass crystallinity ratio values (\Box) as determined from DSC (X_{cDSC}) and α -relaxation temperatures T_{α} at 1950 Hz (\blacksquare) vs. the crystallization temperature (T_c) for samples crystallized during $t_c = 30$ min

3.2. Relaxation Dynamics and nano-scaled morphology

The relaxation phenomena in amorphous and semi-crystalline PEN have been previously investigated by means of dynamic mechanical analysis (DMA) and dielectric relaxation spectroscopy (DRS)⁴⁻⁷. Three relaxation processes: β , β^* and α have been observed in order of increasing temperatures:

- The β -relaxation can be observed at around -20°C for a frequency of 1 kHz. It is similar to the subglass transition of PET and is associated to the localized motions involving the ester groups^{3,7,34,35}.

- The β^* -relaxation, appearing at around 100°C for a frequency of 1 kHz is another sub-glass transition with cooperative feature. This process was assigned to the out of plane motions of the naphthalene cycle by Bellomo *et al.* ³⁶ and more precisely to the motions within nano-scale aggregates of naphthalene rings motions ^{4,6,7,37,38}. In the frequency/temperature region of the β^* process, the contribution of motions within liquid-crystalline nanodomains are also reported after crystallization from the molten state⁴² which can complicate the exact attribution of the β^* process.

- The α -relaxation which appears at around 140°C for a frequency of 1 kHz is associated to the glass transition. Thus, this process is due to cooperative segmental motions in the (mobile) amorphous regions within the lamellar stacks of the spherulites ^{2,10,12,39,40} or in the amorphous zones between spherulites.

The dielectric behaviors of amorphous and cold-crystallized PEN samples are displayed in Figure where $Tan(\delta) = \varepsilon''/\varepsilon'$ is plotted as a function of the temperature for the films crystallized during 24h at 165 and 245°C. The three relaxations described above can be observed. In the crystallization conditions chosen for this study, the temperature location of the β and β^* relaxation peaks are not significantly affected by crystallization, but the value of $Tan(\delta)$ in the entire relaxation pattern is decreased as the cristallinity ratio is increased, *i.e.* the number of mobile dipoles decreases. For the amorphous sample, a cold crystallization peak (CC) occurring at around 175°C can be observed. The occurrence of a $Tan(\delta)$ maximum in the crystallization region is not connected to a specific relaxation process (the temperature at maximum is not affected by frequency), but to a gradual change in the α -relaxation peak shape induced by cold crystallization and resulting confinement of the amorphous phase by the crystalline phase. A magnification in the glass transition region is represented as an onset in Figure The effect of crystallization classically shifts the glass transition relaxation to higher temperatures and also contributes to a broadening of the dielectric relaxation peaks.

A more systematic evolution of the α -relaxation temperature T_{α} at 1950 Hz is shown in Figure 3 (filled squares) displaying the decrease of T_{α} with crystallization temperature T_c . Again, a transition between two confinement regimes can be observed below and above the crystallization temperature 210°C. Theses relaxation results are consistent with the decrease of the calorimetric glass transition temperature with T_c as shown in Figure 1. As a conclusion, the apparent decrease of the glass transition relaxation and calorimetric glass transition temperatures with increasing crystallinity ratios and crystallization temperatures should be connected to the variation of the crystalline morphology and/or the structural state within the amorphous phase with T_c . Further analysis is needed to interpret the confinement effects of the crystalline onto the amorphous phase.



Figure 3: $Tan(\delta)$ as a function of temperature at 1950 Hz for amorphous PEN (**■**) and the samples crystallized during 24 hours at 165 (\Box) and 245°C (∇).

The fine structure of the lamellar stack morphology was studied by Small Angle X-ray Scattering. The values of the long period $L_p = \ell_a + \ell_c$ (deduced from the Bragg equation applied to the Lorentz-corrected SAXS data, see Figure 4), together with ℓ_a and ℓ_c thicknesses deduced from equation 5 and 6 are reported in Table 1 and Table 2

The long period L_p classically increases with crystallization temperature indicating that lamellar stacks with coarser morphology are developed for the high T_c values. In addition, L_p decreases

while the annealing time increases. This could be related to the partial insertion of new lamellae (possibly originating from the slow secondary crystallization) between existing crystallites so that lamellar stacks with smaller average long period progressively develop⁴¹. Such morphology development significantly impacts the dynamics as a result of the additional confinement effects of this new crystalline population.



Figure 4: SAXS diagrams for the amorphous PEN and the samples crystallized during 2 hours at different temperatures.

T_c (°C)	$t_c(h)$	$L_{p}(A)(\pm 3 \text{ Å})$	$\ell_a(\AA)$ (±3 Å)	ℓ_c (Å) (±2 Å)
	0.5	134	100	34
165	2	132	98	33
	24	125	93	32
	0.5	138	102	36
180	2	135	99	36
	24	124	88	36
	0.5	153	109	44
220	2	140	96	44
	24	135	91	44
245	0.5	177	119	58
	2	180	118	62
	24	174	108	66

Table 1: Lamellar stack morphology as determined by SAXS for cold-crystallized samples of PEN as a function of annealing time and temperature.

T_c (°C)	$L_p(Å)$ (±3 Å)	$\ell_a(A)$ (±3 Å)	ℓ_c (Å) (±2 Å)
170	135	100	35
180	138	102	36
190	142	104	37
200	145	106	39
210	147	107	39
220	153	108	44
230	153	109	49
240	169	113	56

Table 2: Lamellar stack morphology as determined by SAXS for the second set of the crystallized samples of PEN as a function of annealing temperature ($t_c = 30 \text{ min}$)

4. Discussion

4.1 Geometrical analysis of confinement

The effect of crystallization on the "characteristic size" of the amorphous phase can first be discussed with the calculation of the amorphous lamellae thickness ℓ_a from SAXS diagrams (yielding L_p) and DSC (X_c) measurements from equation 6. Hence, assuming a localization of the rigid amorphous phase at the interface between crystal and amorphous lamellae, the central thickness $\ell_{a(MAF)}$ of the mobile amorphous fractions could be determined according to the following equation:

$$\ell_{a(MAF)} = (1 - RAF_{DSC})^* \ell_a \tag{5}$$

The corresponding calculations on the basis of Table 2 are ranging between 50 Å ($T_c=180^{\circ}$ C, $t_c=24$ h) to 105Å ($T_c=245^{\circ}$ C, $t_c=30$ min). Such characteristic widths of the MAF need to be compared to characteristic volume of cooperativity at the glass transition (ξ^{3}_{Tg}) calculated by using the Donth approach⁴¹⁻⁴³:

$$\xi_{T_g}^3 = \frac{\Delta(1/C_v)}{\rho(\delta T)^2} k T_g^2 \tag{6}$$

where k is the Boltzmann constant, T_g is the glass transition temperature, $\Delta(1/C_v)$ is the step decrease in the reciprocal specific heat at T_g , ρ is the density of the amorphous material and $(\delta T)^2$ is the mean square temperature fluctuation related to the dynamic glass transition of a Cooperative Rearranging Region. $\Delta(1/C_v)$ can be evaluated by neglecting the difference between the heat capacity step at constant pressure and at constant volume:

$$\Delta(1/C_{\nu}) \approx \Delta(1/C_{p}) = (1/C_{p})_{\text{glass}} - (1/C_{p})_{\text{liquid}}$$
(7)

Thus, for amorphous PEN, a characteristic volume of cooperativity of around 4.1 nm^3 and a characteristic size of around 16 Å (10 Å if a sphere volume is considered) were obtained. These values are significantly lower than the values obtained for the MAF thicknesses in semicrystalline systems exhibiting significant confinement effects. This difference is possibly related to the localization hypothesis: the rigid amorphous fraction may not be limited to the amorphous/crystal interface, but should be extended to any chain with conformation that is unfavourable for mobility, such as the

extended or stretched conformation between two adjacent crystallites. In this view, intercrystalline bridging chain segments or taut tie molecules could be considered to be part of the RAF even if they are not localized into the amorphous/crystal interface. Actually, such tie molecules should be considered as rigid entanglement obstacles for other amorphous chains, so that even if the tie-chain density is low, their effect on the RAF might be significant. The variation of the thermo-mechanical crystallization conditions should then be considered as a way to impact the semicrystalline morphology associated with a resulting tie-molecule density and their confinement effects.

In Figure 5(a) the α -process temperatures (at f = 1950 Hz) are plotted as a function of the respective values of ℓ_a . All the results are fairly rationalized in the $T_{\alpha}|_{f=1950\text{Hz}}$ - ℓ_a plot, where the values of T_{α} appear largely impacted by the amorphous widths ℓ_a . It can be observed again that as the crystallization temperatures increase, a higher mobility is observed due to the increase of the width of the amorphous lamellae. Moreover, for the same crystallization temperature, as the annealing time increases, the molecular mobility decreases due to secondary crystallization inducing a lower value of ℓ_a . Yet, the morphology of the samples crystallized for a longer time (24 h) is related to the crystallization temperature close to 220°C (see Figure 5a, up triangle empty symbols), as a result of the combined effects of the initial lamellar stack morphology and the subsequent refinement of the microstructure induced by secondary crystallization as described by Strobl *et al*⁴⁴. As a result, the values of ℓ_a do not seem to follow the same evolution for long crystallization times in comparison with the samples crystallized during 30 minutes where ℓ_a monotonously increases as the crystallization temperature increases (see Figure 5a, dark gray symbols and black symbols) but with a step-like evolution close to the crystallization temperature of 210°C.



Figure 5: (a) α -process temperatures $(T_{\alpha}) (\pm 0.5^{\circ}\text{C})$ as a function of the amorphous layer length (ℓ_{a}) for the samples crystallized at $T_{c} = 165 (\Box)$, 180 (\circ), 220 (Δ) and 245°C (∇). The open symbols correspond to a crystallization time (t_{c}) of 24 h, the grey symbols to $t_{c} = 2$ h and the dark grey and black symbols (\blacksquare) to $t_{c} = 30$ min. (b) α -process temperatures $(T_{\alpha}) (\pm 0.5^{\circ}\text{C})$ as a function of the characteristic length $(2^{*} \ell_{c} + \ell_{a})$ (same symbols as in (a)).

4.2 Role of tie-molecules in the confinement effects.

Although a purely geometrical approach of confinement based on equations 5 and 6 does not yield alone a satisfactory frame of interpretation of the confinement effects in semicrystalline PEN, the evolution of the glass transition dynamics with semicrystalline morphology or crystallization temperature/time can be discussed invoking the role of tie molecules. In particular, the effect of the

crystallization temperature can be first related to the tie molecule density through the degree of regular folding at the surface of the crystallites. Indeed, the works of Hoffman *et al.* $^{46-48}$ have shown that in the high crystallization temperature range, regular folding is facilitated by thermal activation, contrarily to lower crystallization temperatures. Thus, a higher number of tie molecules is expected to emerge from the crystals in order to connect the lamellar stacks in the samples crystallized at low temperatures. Another issue is the intrinsic effect of the crystal thickness and interlamellar spacing on the density of the tie molecules. Experimentally, the tie molecule density is known to decrease sharply with increasing long period L_p^{49} . The relation between the tie molecule density, mean gyration radius of the chains and semicrystalline morphology parameters (L_p, ℓ_c, ℓ_a) was formalized in the theory of Huang and Brown⁵⁰⁻⁵¹ and illustrated in a variety of experimental investigations⁵². Accordingly, the increase of the characteristic length $2\ell_c + \ell_a$ decreases the probability to form a tie-chain molecule: a tie molecule is formed if the end-to-end distance of the random coil (before crystallization, in the melt) is larger than the critical length $2\ell_c + \ell_a$ (after the lamellar stacks are formed in the semicrystalline state). An illustration of the role of the characteristic length $2\ell_c + \ell_a$ is given in Figure 5(b), although longer crystallization/annealing times clearly yield to confinement laws slightly shifted to higher T_{α} values. This is indication that the semicrystalline morphology could be more complex than the description proposed in the frame of the lamellar stack model: the development of small non-lamellar crystals within the amorphous layers by secondary crystallization could have negligible impact on the mean long period as deduced by SAXS, but could significantly contribute to confinement effects by physical cross-linking. Such complex morphology could also explain the asymmetry towards the large q range tail of the SAXS patterns (see Figure 4). The effect of the crystallization temperature or annealing time was previously related to the RAF due to crystalline defects removal⁵³ in the case of PET: the decrease in the RAF is attributed to crystal perfection enhancement which in turn decreases the strain transmitted to the amorphous phase by means of the tie molecules⁵⁴. In the present work, the increase of the crystallization temperature is indeed observed to induce a higher crystalline perfection, but it also leads to an increase of the crystallinity ratio (see Figure 2) that should increase the number of tiechain molecule between the primary crystalline lamellae and the newly formed secondary crystalline entities. In the same way, increasing the annealing or crystallization time systematically induces an increase of the confinement effects as a result of crystallization and subsequent a decrease of L_p and ℓ_a , although no increase of the crystalline perfection could be evidenced from X-ray diffraction measurements. A rather unexpected result was observed for the samples crystallized during 30 minutes at 240 and 245°C. The α -process temperature (f = 1950 Hz) of these sample were comparable to the amorphous sample (see Figure 5b), in spite of the presence of the crystalline phase. This should be related to a lower entanglement density in the amorphous lamellae.

To go a step further, we have evaluated the optimal structural length ℓ^* connected to the glass transition dynamics, in the form of:

$$\ell^* = (\ell_a + k. \ \ell_c) / (1 + k) \tag{8}$$

where k was adjusted to find minimum dispersion around the general trend curve of the T_{α} - ℓ^* plot (for details of the numerical see supplementary material). The optimal result accounting for all the results is found for k=0.83 corresponding to an intermediate result between $\ell^* = \ell_a$ and $\ell^* = (\ell_a + 2 \ell_c)$ (see Figure 5a), but close to the value of $\ell^* = L_p$. Such critical length scaling with L_p was invoked in previous works^{55,56} for the estimation of tie molecule density, which can be interpreted as an indication of the important role of tie molecule density in the confinement effects of the glass transition in semicrystalline polymers. The optimal plot is thus given in Figure 6. Here again, the high temperature crystallization data at $T_c=245$ °C cannot be renormalized on the common pattern. In this temperature range, the evolution of T_{α} at 1950Hz should thus be governed by additional disentanglement processes that should be disconnected to semicrystalline morphology.

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Figure 6: α -process temperatures $(T_{\alpha}) (\pm 0.5^{\circ}\text{C})$ as a function of the critical length $\ell^* = \ell_a + k \ell_c / (1+k)$ where k=0.83. The open symbols correspond to a crystallization time (t_c) of 24 h., the grey symbols to $t_c=2$ h and the dark grey and black symbols (\blacksquare) to $t_c=30$ min.

5. Conclusion

The effect of confinement of the amorphous phase by the crystalline nanophase in semi-crystalline PEN after crystallization in large temperature and crystallization time ranges has been studied. The evolution of the molecular mobility is shown to be largely impacted by the tie molecule density that is in turn related to the semicrystalline morphology. Such tie molecules should be considered as rigid entanglement obstacles for other amorphous chains, so that even if the tie-chain density is low, their effect on the glass transition dynamics and the RAF is significant. Accordingly, the characteristic length optimally describing the structural evolution of the dielectric glass transition relaxation was found to be $1^*=1_a+0.83 \ l_c \sim L_p$, where L_p is the long period, l_a is the inter-crystalline distance and l_c the crystalline thickness. At high crystallization temperatures (above 220°C) additional effects with the degradation of the polymer chains should be considered, leading to a decrease of the entanglement and tie molecule density and thus to lower confinement effects. Such analysis explains why the evolution of the frequency/temperature location of the dielectric α -relaxation peak should not be directly related to the crystallinity ratio but depends on the details of the crystalline lamellar stack morphology governing the tie-molecule density.

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