Dependence of conformational relaxation on nanoconfinement in semicrystalline poly(ethylene terephthalate)

M. Pieruccini^{1,*}, A. Flores² and F.J. Baltá-Calleja²

¹ *CNR, Istituto di Nanoscienze, v. Campi 213/A, 41125 Modena, Italy and*

² *Instituto de Estructura de la Materia,*

CSIC, Serrano 119, 28006 Madrid, Spain

PACS: 61.41.+e, 61.05.cp, 64.70.Nd

Short title: **Nano-confinement vs. relaxation in PET**

Abstract

Some new aspects concerning the mechanical response of amorphous regions confined by crystals in nano-sized domains are illustrated for semicrystalline poly(ethylene terephthalate) (PET), on the basis of indentation hardness and dynamical mechanical spectroscopy (DMS) analyses ($10^{-3} \div 60$ Hz frequency range for DMS). Samples were crystallized from the glassy state at low and high temperatures ($T_c = 100$ °C and 160 °C, respectively) and subsequently recrystallized some degrees above to gain information on the nature of the amorphous regions. DMS reveals two segmental relaxation processes ascribed to the interlamellar amorphous regions (slow mode) and to the inter-stack amorphous pockets (APs) (fast mode), the latter being the object of the present study. It is shown that recrystallization changes the cooperativity within the APs. At low T_c , an increase in the cooperativity and the free energy barrier for readjustment is found after recrystallization. Concurrently, the average value of the hardness of the amorphous regions, H_a , (derived using the hardness additivity law) is found to increase. The reduced size of the APs regions upon recrystallization is discussed as a relevant parameter giving rise to an enhanced segmental confinement and a parallel hardening. Results for the high T_c material reveal that, in this case, both the cooperativity and H_a decrease upon recrystallization. This result highlights the large influence of the coupling of the APs with the crystal walls on the relaxation mode and in turn the mechanical behavior of the material.

I. INTRODUCTION

Understanding how nanoconfinement affects the bulk properties of physical systems is of extreme importance from the viewpoints of both basic Physics and related technological aspects. In Polymer Science, the relevance of the nano-confinement of the amorphous domains in the overall mechanical and dielectric responses has been addressed in preceding studies [1–4]. Poly(ethylene terephthalate) (PET) has been frequently employed to contrast experimental observations with a number of models developed to understand the nature of the amorphous regions.

At the end of the crystallization process, nano-sized amorphous domains remain embedded by the crystals [5]. In these conditions, a sort of crystal/amorphous equilibrium is established and the thermodynamic state of the amorphous regions necessarily carries information about the thermodynamic state of the embedding crystals [3]. The latter can be easily described [6] and hence, this scenario offers some advantage with respect to the study of polymers confined in other media such as for example in nanoporous glasses (see e.g. [7]).

Isothermal crystallization processes lead to the formation of lamellar stacks with morphological features characteristic of the crystallization conditions. Upon further heating, the stacks loose stability, which may be subsequently recovered by re-crystallizing into new lamellar stacks with different crystalline and amorphous layer thicknesses. For instance, in case of PET crystallized from the glassy state, a low-temperature melting endotherm appearing a few degrees above the crystallization temperature is frequently associated to recrystallization processes (see e.g. Fig. 1 in ref. [8]).

The aim of the present study is to explore the influence of recrystallization processes on the mechanical performance of PET as a consequence of variations in the confinement of the amorphous regions by the lamellar crystals. For this purpose, PET crystallized from the glassy state at two different temperatures (100 °C and 160 °C) and further recrystallized in the vicinity of the respective low-temperature melting endotherms will be explored. Indentation hardness will be used to evaluate differences in the mechanical properties of the amorphous regions induced by the various thermal treatments. This technique has been proved to be extremely sensitive to changes taking place in glassy polymer domains such as those arising from physical ageing processes, chain orientation effects, occurrence of local internal order, etc [9, 10]. In addition, dynamic mechanical spectroscopy (DMS) analysis will

be employed to extract information on the extent of segmental confinement within the amorphous regions upon recrystallization. Indentation hardness and spectroscopy measurements will be comprehensively discussed in the light of the structural information provided by means of wide-angle X-ray diffraction and with the help of preceding published small-angle X-ray diffraction data.

II. EXPERIMENTAL

Glassy PET from Goodfellow (ES 301465) with molecular weight $M_w \sim 20,000$ g/mol was purchased in form of films of 0.5 mm thickness. Portions of the films were crystallized in inert atmosphere at either $T_c = 100$ °C or 160 °C for 7 h. The specimens were investigated without further treatment and also after recrystallization at 115 °C or 125 °C in case of the sample crystallized at 100 °C, and at 175 °C and 185 °C for the material crystallized at 160 °C. All recrystallization treatments were applied under vacuum for a period of 2 h.

Wide-angle X-ray scattering (WAXS) measurements were carried out at room temperature using a Micro Star rotating anode generator with copper target manufactured by Bruker (Germany). WAXS patterns were recorded using a Mar345 image plate with a resolution of 3450×3450 pixels and $100 \mu\text{m}/\text{pixel}$; a sample-to detector distance of 200 mm was used. Isotropic rings associated to the diffraction maxima were obtained for all the samples. In case of the untreated PET sample, an amorphous halo characteristic of the glassy material was obtained. All patterns were azimuthally integrated using the FIT2D software package in order to obtain intensity curves as a function of diffraction angle [11]. The degree of crystallinity, α_{WAXS} , was estimated by fitting the amorphous halo of glassy PET to the diffraction curve of each crystallized material. The α_{WAXS} values were determined from the ratio of the area under the crystalline peaks to that of the total diffraction curve.

Microindentation measurements were carried out at room temperature using a Vickers diamond attached to a Leica tester. The indenter penetrates the sample surface at a given load, P , for a short period of time (6 s) to minimize creep effects. The diagonal of the residual impression, d , left behind upon load release, is measured using an optical microscope. Microhardness values, H , are derived following:

$$H = 1.85 \frac{P}{d^2} \quad (1)$$

A load of $P = 0.98$ N was employed. Indentations with diagonal lengths in the range of $100\text{ }\mu\text{m}$ were obtained. Microhardness values were determined from the measurement of at least 8 indentations.

Isothermal DMS analysis was performed with a TRITON Technology Analyser in the frequency interval of $10^{-3} \div 60$ Hz in bending mode, single cantilever configuration.

III. RESULTS

A. Microhardness

Table I reports the structural data of the stacks (i.e. thickness of the crystal lamellae, l_c , of the interlamellar amorphous layers, l_a , and the long period $L = l_c + l_a$) measured at room temperature by means of small angle X-ray diffraction on samples crystallized for 7-9 h at either $T_c = 100\text{ }^\circ\text{C}$ or $T_c = 160\text{ }^\circ\text{C}$ before and after recrystallization [4, 8]. Samples crystallized at $100\text{ }^\circ\text{C}$ were further recrystallized at $115\text{ }^\circ\text{C}$ and $125\text{ }^\circ\text{C}$ for 2 h, while recrystallization temperatures of $175\text{ }^\circ\text{C}$ and $185\text{ }^\circ\text{C}$ were chosen for the $T_c = 160\text{ }^\circ\text{C}$ samples. The l_c and l_a data in Table I were estimated from the analysis of the Interface Distribution Function [8]. The crystallinities determined by wide angle X-ray scattering, α_{WAXS} , as well as the degree of crystallinity within the lamellar stacks ($\alpha_L \equiv l_c/L$) are also reported in the table.

The room temperature microhardness values, H , of all the samples investigated, H , are listed in Table II, together with the hardness of the amorphous domains, H_a , determined using the well-established additive model:

$$H = \alpha_{WAXS}H_c(l_c) + (1 - \alpha_{WAXS})H_a \quad (2)$$

where H_c is the hardness value of the crystals of thickness l_c and can be estimated as described below. The validity of eq. 2 relies on the fact that plastic deformation takes place both in the crystalline and in the amorphous regions. The additive model has been successfully employed to explain the mechanical behaviour of a wide range of polymer materials [9, 10]. On the other hand, there is also sound experimental evidence that the crystal thickness modulates the hardness of a polymer material [9, 10]. Baltá-Calleja and Kilian were the first to propose a model of destruction of crystal blocks during an indentation cycle

PET Sample	l_c	l_a	L	α_L	α_{WAXS}
	(nm)	(nm)	(nm)		
Cryst. 100 °C	2.9	3.9	6.8	0.43	0.26
Re-cr. 115 °C	3.5	3.8	7.3	0.48	0.28
Re-cr. 125 °C	2.7	4.3	7.0	0.39	0.29
Cryst. 160 °C	3.7	4.7	8.4	0.44	0.33
Re-cr. 175 °C	3.9	4.7	8.6	0.45	0.34
Re-cr. 185 °C	2.8	5.2	9.0	0.42	0.36

TABLE I: Lamellar and interlamellar thicknesses, l_c and l_a respectively, long period $L = l_c + l_a$ and linear crystallinity $\alpha_L \equiv l_c/L$ of PET samples crystallized at either $T_c = 100$ °C or $T_c = 160$ °C for 9 h and subsequently recrystallized for 2 h at either 115 or 125 °C for the low- T_c sample and at either 175 or 185 °C for the high- T_c one (data from refs. [4, 8]).

that explains the observed hardness variation with crystal thickness. The model arrives to the following relationship between H_c and l_c [10]:

$$H_c = \frac{H_c^\infty}{1 + b_H/l_c} \quad (3)$$

where H_c^∞ is the hardness of an infinitely thick crystal mainly related to crystal chain packing density and b_H is a parameter related to the surface free energy of the crystal, σ , and to the energy Δh required for plastic deformation of the crystal blocks: $b_H = 2\sigma/\Delta h$. Equation 3 has been tested for a number of semicrystalline polymers including flexible polyolefins and semirigid polyesters. In case of PET, preceding studies suggest that $H_c^\infty = 400 \div 420$ MPa [9] and $b_H \approx 1$ nm [12]. Using eq. 3 with $H_c^\infty = 418$ MPa, $b_H = 1$ nm and the l_c values of Table I, one can calculate H_c for each sample and introduce this value into eq. 2 to derive the H_a values collected in Table II (see also ref. [13]).

It is noteworthy that H_a depends not only on the crystallization temperature but also on the subsequent recrystallization process. Indeed, a clear H_a enhancement is observed when increasing the crystallization temperature from 100 °C to 160 °C. Moreover, for the low crystallization temperature, H_a increases upon recrystallization at 115 °C and a further H_a enhancement seems to take place when the recrystallization temperature raises up to 125 °C. In contrast, a H_a decrease is detected when additional thermal treatments are applied to

PET Sample	H	H_a
	(MPa)	(MPa)
Cryst. 100 °C	166±3	115
Re-cr. 115 °C	178±4	121
Re-cr. 125 °C	183±3	133
Cryst. 160 °C	196±4	131
Re-cr. 175 °C	194±3	122
Re-cr. 185 °C	199±4	126

TABLE II: Room temperature H values of the PET samples crystallized at $T_c = 100$ °C or 160 °C for 7 h and subsequently recrystallized at the indicated temperatures for 2 h (see ref. [13] for the low- T_c data). The average hardness values of the amorphous regions were derived using eq. 2.

samples crystallized at high temperatures. Results suggest the occurrence of some structural changes within the amorphous regions specific for each thermal treatment.

B. Dynamic mechanical spectroscopy

Dynamic mechanical spectroscopy analysis shows that in the present frequency range the elastic modulus E is composed of two segmental relaxation processes: a slow one ascribed to the interlamellar amorphous regions within the stacks and a fast one associated to inter-stack amorphous pockets (APs) [13, 14]. They are both described by a symmetric Havriliak-Negami process (or Cole-Cole):

$$E = \sum_{k \equiv s, f} \frac{A_k}{1 + (i \omega \tau_{k0})^{a_k}} \quad (4)$$

with A_k the amplitude of the k -th process (s and f standing for "slow" and "fast" respectively), τ_{k0} its central relaxation time, ω the angular frequency and a_k the width parameter.

Figure 1 shows the overall mechanical patterns of the imaginary part E'' of the elastic modulus at $T = 95$ °C for the $T_c = 100$ °C samples before and after the recrystallization processes. For the non-recrystallized sample, the decomposition into fast and slow modes is also shown.

We observe that in this case recrystallization causes an overall downwards frequency shift

FIG. 1: Imaginary part of the mechanical modulus E'' at $T = 95$ °C, as a function of the frequency, for a PET sample crystallized at $T_c = 100$ °C and subsequently recrystallized. The solid line is the fitting curve resulting from the superposition of two symmetric Havriliak-Negami processes labelled as Fast and Slow, represented by dashed lines for the non-recrystallized sample. (Replotted from ref. [13])

FIG. 2: Same as Fig. 1, $T = 95$ °C, for a PET samples initially crystallized at $T_c = 160$ °C.

of the pattern, denoting an increase in the rigidity of the amorphous regions. This behavior has been discussed in ref. [13].

Figure 2 reports analogous results as those included in Fig. 1 for the samples crystallized at $T_c = 160$ °C. In this case we find that recrystallization causes a slight upwards frequency shift of E'' , denoting an increase of the average segmental mobility.

The fast mode component in the high- T_c sample is always better defined than the slow mode one and for this reason the present work focuses in the analysis of the former. However, inspection of the slow mode allows us to conclude that a_s is significantly lower in the $T_c = 160$ °C samples than in the low- T_c ones (typically 0.15 against 0.25). This is indicative that the segmental dynamics within the stacks of the high- T_c samples is considerably more restricted [14].

Table III reports relevant parameters characterizing the fast relaxation mode for selected samples.

Confinement confers to the segmental dynamics a character of cooperativity, which means that conformational changes are possible provided *i*) a sufficient number of monomers concur to the motion and *ii*) thermodynamic fluctuations of sufficient energy occur [15]. These monomers form what is called a static cooperatively rearranging region (SCRR) [2]; its conformational relaxation rate is itself characterized by fluctuations. For this reason the frequency spectrum associated to the conformational motion of an ensemble of SCRRs is significantly broad; indeed, its width increases with the height of the (average) rearrangement free energy barrier [2]. At a given time, each SCRR can be characterized by its own, actual value of a constraint parameter ζ , i.e. the minimum fluctuation energy (per monomer), capable to induce a conformational change. In order to change state (i.e. ζ), a SCRR has to cross a free energy barrier $\Delta F = z \Delta\mu$, with z the number of monomers in a SCRR and

$$\Delta\mu = -k_B T \ln \left[\frac{Z(\zeta)}{Z_0} \right], \quad (5)$$

with $k_B T$ the thermal energy; the reduced partition function

$$Z(\zeta) \propto \int_{\zeta}^{\infty} dE E^n e^{-E/k_B T} \quad (6)$$

is the sum of just the (single-monomer) states through which a conformational transition may take place, and $Z_0 = Z(\zeta)|_{\zeta=0}$. In eq. 6, n controls the density of (mobility) states. The lifetime of a SCRR in a state ζ is thus

$$\tau(\zeta) = \tau^* e^{z\Delta\mu(\zeta)/k_B T}, \quad (7)$$

with z the number of monomers of which the SCRR is made and τ^* is the characteristic time of the attempts of the heat bath to induce conformational transitions by fluctuations.

The relaxation function of an ensemble of SCRRs populating the ζ space with a distribution $p(\zeta)$, is thus given by

$$\phi(t) = \int_0^\infty d\zeta p(\zeta) \exp \left\{ -\frac{t}{\tau^*} e^{-z \Delta\mu(\zeta)/k_B T} \right\}. \quad (8)$$

Equation 8 means that the overall relaxation dynamics of an ensemble of SCRRs is the superposition of independent single-time decays and is the formal translation, in our two-point correlation function, of the concept of dynamical heterogeneity [16]. The problem of finding $p(\zeta)$ has been addressed in ref. [2] and the result is a quasi-poissonian distribution:

$$p(\zeta) \sim e^{-\lambda \Delta\mu(\zeta)}, \quad (9)$$

where λ is a Lagrange multiplier associated to the condition that the average rearrangement chemical potential barrier

$$\overline{\Delta\mu} \equiv \int_0^\infty d\zeta p(\zeta) \Delta\mu(\zeta) \quad (10)$$

must be stationary.

The frequency width a_f of the relaxation is determined by the dispersion $\delta[\Delta\mu]$ around the mean $\overline{\Delta\mu}$ [14]. On the other hand, the quasi-poissonian character of $p(\zeta)$ implies that

$$\delta[\Delta\mu] \approx \overline{\Delta\mu}; \quad (11)$$

thus, assuming that in the present measurements the a_f is (almost) totally determined by this dispersion [14], it is possible to extract information on $\overline{\Delta\mu}$ (and z as well) from the curves of Figs. 1 and 2, by fitting the associated relaxation functions with eq. 8.

Following a procedure described in detail in [2, 13, 14], the parameters listed in Table III were found.

IV. DISCUSSION AND CONCLUSIONS

The measurements carried out on the non-recrystallized samples indicate that both the cooperativity z and ΔF are larger for the high- T_c sample (independently of the measurement temperature), suggesting an enhancement of dynamical restrictions. At the same time, by comparing the degrees of crystallinity in the bulk and in the lamellar stacks (α_{WAXS} and α_L in Table I, respectively) it is found that the fraction of material within the APs, i.e. $1 - \alpha_{WAXS}/\alpha_L$, is significantly lower in the high- T_c sample. This would suggest a smaller

PET Sample	T	τ_f	a_f	τ^*	z	$\overline{\Delta\mu}$	$\delta[\Delta\mu]$	ΔF
	(°C)	(s)		(s)		kJ/mol	kJ/mol	kJ/mol
Cryst. 100 °C	85	50	0.31	2.5×10^{-3}	11.3	2.39	1.30	27
	95	3.5×10^{-2}	0.37	5.3×10^{-4}	3.6	5.65	3.43	20.4
Re-cr. 115 °C	95	5.6×10^{-2}	0.35	6.4×10^{-5}	3.9	5.48	3.39	21.3
Re-cr. 125 °C	95	8.8×10^{-2}	0.32	4.0×10^{-5}	4.9	4.86	2.97	23.7
Cryst. 160 °C	85	26	0.29	$< 5.3 \times 10^{-4}$	> 13	(2.35)	(1.26)	> 29.4
	95	3.5×10^{-2}	0.29	1.4×10^{-6}	7	4.33	2.35	30.9
Re-cr. 175 °C	95	2×10^{-2}	0.37	1.2×10^{-5}	4	5.63	3.1	22.4
Re-cr. 185 °C	95	1.5×10^{-2}	0.37	2.6×10^{-5}	3.7	5.54	3.36	20.3

TABLE III: Fast mode central relaxation times τ_f and widths, a_f , for samples crystallized at $T_c = 100$ °C before and after recrystallization at either 115 or 125 °C (data from ref. [13]) and for samples crystallized at $T_c = 160$ °C before and after recrystallization at either 175 or 185 °C. T is the temperature of measurement. See text for the other relaxation parameters. (The analysis of the $T_c = 160$ °C sample data at 85 °C was difficult and only approximate results are reported.)

size of the APs, giving rise to a more effective confinement by the adjacent crystals and hence, to an enhanced cooperativity. Besides, the idea that smaller APs form at higher T_c hints at the possibility that their size depends on that of the SCRRs: smaller SCRRs could allow for smaller APs to be formed at high T_c (this is supported by the fact that the density autocorrelation length in a melt decreases with increasing T [1, 17]). Since the SCRR size increases on cooling [13, 14], a lowering of the temperature in an already crystallized sample (such as the $T_c = 160$ °C one) could result in a decrease of the AP/SCRR size ratio as an additional contribution to the observed increase of rigidity.

On the other hand, a clear enhancement of H_a in the high- T_c material is observed (see Table II). This could also be related to the fact that only approximately 25% of the total fraction of amorphous material remains in the APs, with respect to 40% in case of the low- T_c sample. The average H_a values collected in Table II result from the contribution of both, the amorphous material within the lamellar stacks and that within the APs. One would expect higher hardness values for the former with respect to the latter due to a more effective

confinement by the crystals [13, 14]. This would explain the evident H_a enhancement for the high- T_c sample where a larger fraction of the total amorphous material resides between the crystal lamellae.

Recrystallization processes are found to significantly change all the parameters of the DMS analysis. Indeed, measurements at 95 °C on the low- T_c sample reveal an increase in z and ΔF due to recrystallization at both 115 °C and 125 °C (see Table III). This has been discussed in ref. [13] and in the present context it can be viewed as a consequence of a more effective coupling of the APs with the confining crystal walls. It is noteworthy that the amount of material within the APs decreases significantly for the material recrystallized at 125 °C (see the α_L and α_{WAXS} values in Table I) which exhibits the largest differences in z and ΔF . Smaller size of the APs would promote enhanced confinement by the neighbouring crystals. A clear increase of the average H_a values upon recrystallization at 115 °C and 125 °C is observed concurrently to the changes detected by means of DMS. On the one hand, the suggested enhanced confinement within the APs would promote a hardness enhancement; on the other, a lower fraction of amorphous material outside the lamellar stacks would yield a higher average H_a as a consequence of a smaller contribution of the "softer" interstack amorphous phase with respect to the "harder" amorphous interlamellar phase. Finally, it should also be noted that structural changes within the lamellar stacks take place upon recrystallization (see Table I). The mechanisms associated to these changes were carefully discussed in refs. [4, 13] for each recrystallization temperature concluding that in all cases a stiffer amorphous interlamellar phase could be envisaged, hence, in agreement with the present findings.

In contrast, DMA analysis of the high- T_c samples shows (see Table III) that cooperativity reduces from $z = 7$ to $z \simeq 4$ after recrystallization and, correspondingly, also ΔF ; moreover, a slight acceleration is observed in the overall relaxation dynamics (cf. the τ_f values). This points towards an apparent reduction in the coupling of the amorphous molecules to the crystal walls, although a slight decrease of density within the APs after recrystallization cannot be excluded [we note that the acceleration of the dynamics is accompanied by a narrowing of the relaxation, to be compared to the case of poly(dimethyl siloxane) confined in silanized nanopores [7, 18, 19], where the acceleration observed on decreasing the pore size is paralleled by a broadening of the process; see ref. [14] for a discussion]. The result is also consistent with a mechanism involving a local relaxation of the orientation of amorphous

molecules, for example, upon the release of internal stresses. Most interesting is the fact that H_a shows a tendency to decrease after recrystallization at 175 °C and 185 °C [note the decrease in H_a after 175 °C recrystallization, paralleled by the decrease in cooperativity, at an almost constant fraction of amorphous material in the APs; this supports the assumption of a fast mode width a_f entirely due to $\Delta\mu$ (see eq. 11), as the basis of the DMS data analysis; cf. [14]]. In fact, comparison of the H_a values of Table II with those of ΔF in Table III reveals that these magnitudes follow the same behavior, not only upon recrystallization for a given crystallized sample, but also when comparing variations for different crystallization temperatures (note that this correspondence is not *a priori* obvious since, contrary to the case where microhardness is probed, DMS operates in the linear response regime). This observation highlights the importance of the nature of the APs for the understanding of the mechanical behavior of the amorphous regions and consequently of the bulk material. In case of the high- T_c sample, the enhanced mobility detected within the APs upon recrystallization mediates the expected average H_a enhancement due to an increase of the fraction of amorphous material inside the lamellar stacks (especially at a recrystallization temperature of 185 °C) and a stiffening of the amorphous interlamellar layers arriving from the structural changes shown in Table I and discussed in ref. [13]. As a consequence of the balance of these effects, the average H_a values do not increase upon recrystallization but even exhibit a slight decrease.

In conclusion, the reported analysis seems to indicate that an acceleration or a slowing down of the fast mode relaxation dynamics is accompanied by corresponding changes in the cooperativity, the latter largely influenced by the coupling of the APs with the domain walls (what is called "adsorption effect" [7, 18, 19]). Most interesting is the good agreement found between the DMS results and the indentation measurements reflected in the concurrent variation of the average hardness of the amorphous regions with the changes in cooperativity. Finally, the present results suggest that PET represents a suited system for the investigation of effects at the borders of the APs by just resorting to appropriate thermal treatments.

V. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Ministerio de Ciencia e Innovación Grant No. FIS2010-18069, Spain, for the financial support of this investigation. F.J.B.C. also wishes

to acknowledge the Alexander von Humboldt Foundation for the generous support during this work. M.P. gratefully acknowledges MCYT for the award of a sabbatical grant (SAB-2006-0077) to work at IEM, CSIC, Madrid, for the development of the new method used for relaxation data analysis and CNR, Italy, for supporting this initiative within the framework of "Congedi per Motivi di Studio". We are also indebted to the Department of Crystallography (Instituto de Química-Física "Rocasolano", CSIC) for providing the facilities to carry out the wide-angle X-ray diffraction experiments.

-
- [1] F. J. Baltá Calleja, A. Flores, G. Di Marco and M. Pieruccini, Phys. Rev. B **75**, 224201 (2007); (2009) Phys. Rev. B **79**: 019903
 - [2] M. Pieruccini, T. A. Ezquerra, Eur. Phys. J. E **29**, 163 (2009)
 - [3] M. Pieruccini, A. Flores, Coll. Polym. Sci. **288**, 365 (2010)
 - [4] M. Pieruccini, A. Flores, U. Nöchel, G. Di Marco, N. Stribeck and F. J. Baltá Calleja, Eur. Phys. J. E **27**, 365 (2008)
 - [5] G. Strobl, *The Physics of Polymers*, 2nd ed. (Springer, New York, 1997).
 - [6] J.D. Hoffman, J. Chem. Phys. **29**, 1192 (1958)
 - [7] A. Schönhals, H. Goering, Ch. Schick, B. Frick, R. Zorn, J. Non-Cryst. Solids **351**, 2668 (2005)
 - [8] A. Flores, M. Pieruccini, U. Nöchel, N. Stribeck, F.J. Baltá-Calleja, Polymer **49**, 965-973 (2008)
 - [9] A. Flores, F. Ania, F.J. Baltá-Calleja, Polymer **50**(3), 729-746 (2009).
 - [10] F.J. Baltá-Calleja, S. Fakirov, *The microhardness of polymers*, Cambridge University Press (Cambridge, 2000).
 - [11] A.P. Hammersley, S.O. Svensson, A. Thomson, Nucl. Instrum. Meth. A **346**, 312-321 (1994).
 - [12] A. Flores, M. Pieruccini, N. Stribeck, S. S. Funari, E. Bosch, F.J. Baltá-Calleja, Polymer, **46**(22), 9404-9410 (2005).
 - [13] A. Flores, F. J. Baltá Calleja, G. Di Marco, S. Sturniolo and M. Pieruccini, Polymer **52**, 3155 (2011)
 - [14] P. Calandra, S. Sturniolo, M. Pieruccini, Therm. Acta **522**, 135 (2011)
 - [15] G. Adam, J.H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
 - [16] H. Sillescu H, R. Böhmer, G. Diezemann, G. Hinze, J. Non-Cryst. Solids **307310** 1623 (2002)

- [17] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, Oxford University Press, Oxford, 1998.
- [18] A. Schönhals, H. Goering, Ch. Schick, B. Frick, R. Zorn, Eur. Phys. J. E **12**, 173 (2003)
- [19] B. Frick, C. Alba-Simionesco, G. Dosseh, C. Le Quellec, A.J. Moreno, J. Colmenero, A. Schönhals, R. Zorn, K. Chrissopoulou, S.H. Anastasiadis, K. Dalnoki-Veress, J. Non-Cryst. Solids **351**, 2657 (2005)