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Simultaneous crystalline-amorphous phase evolution during crystallization of polymer systems

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Abstract. – Despite the fact that polymer crystallization has been the object of intense research, this process is far from being fully understood. Traditional polymer crystallization studies using X-ray scattering techniques mainly provide information about the ordered regions. To obtain a more complete information about the time evolution of both the crystalline and the amorphous phase during polymer crystallization, we have developed a technique which allows one to obtain information about both the crystalline and the amorphous phase simultaneously. We report here simultaneous information about three key aspects of the isothermal polymer crystallization process: i) polymer chain ordering, through Wide-Angle X-ray Scattering; ii) lamellar crystals arrangement, through Small-Angle X-ray Scattering; iii) amorphous phase evolution through dielectric spectroscopy. Our results probe that during primary crystallization the average mobility of the amorphous phase is not notably affected. Upon passing through the crossover time, marking the transition from primary to secondary crystallization, the restriction to the mobility of the amorphous phase mainly occurs in the regions between the lamellar stacks and not in the amorphous regions within the lamellar stacks. We hypothesize that molecular mobility in the amorphous regions located between consecutive crystals become strongly arrested as soon as the lamellar stack is formed.

Polymer systems may develop a characteristic folded chain crystalline lamellar morphology at the nanometer level upon thermal treatment within the temperature range between the glass transition temperature, T_g , and the equilibrium melting temperature, T_m^0 [1,2]. The lamellar morphology consists of stacks of laminar crystals and amorphous regions intercalated between them. Although extended chain crystals are thermodynamically more stable, a kinetic factor induces that polymer chains fold many times building up thin (10–20 nm) crystal lamellae. For semicrystalline polymers, this characteristic crystalline nanostructure acts as an internal backbone in the polymer controlling the final mechanical properties of the material.

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For example, if polyethylene, one of the most common polymers (with T_g below room temperature) had not the contribution of the crystalline lamellae, then it would behave at room temperature as a viscoelastic liquid [3, 4]. Despite the fact that polymer crystallization has been the object of research for more than forty years [2], this process is far from being fully understood. In addition to the formation of crystalline lamellae, recent experiments reveal that polymer crystallization involves the development of other nanostructures whose detection is, eventually, within the limits of the present experimentation capabilities [5–11]. Recently, new models have been developed that envision crystallization either from the molten state [12] or from solution [13] as a multi-step process. Synchrotron radiation offers the possibility to combine in a simultaneous fashion small- and wide-angle X-ray scattering (SWAXS) rendering structural information about lamellar stacking and lattice formation in real time [14, 15]. X-ray scattering techniques can also be used to extract structural information in amorphous materials [16]. Owing, however, to the fact that in semicrystalline systems the ordered regions provoke strong diffraction phenomena, superimposed over a relatively weak contribution of the amorphous phase, mainly information about the ordered regions is obtained. To obtain more complete information about the time evolution of both the crystalline and the amorphous phase during polymer crystallization, we have developed a technique consisting in the simultaneous measurement of SWAXS and dielectric spectroscopy (DS) (to be called (SWD) [17]). We exploit the fact that the dynamics of the α -relaxation due to the segmental motions above T_g is strongly affected by the progressive development of the crystalline phase [18–21]. Previous attempts of combining X-ray scattering measurements, over particular spatial ranges, and dielectric spectroscopy were shown to be useful to characterize changes occurring during the induction time for crystallization [22]. The aim of this communication is to present novel results of a crystallizable model polymer (poly(ethylene terephthalate, PET) using the new technique of SWD. We report for the first time simultaneous information about three key aspects of the isothermal polymer crystallization process: i) polymer chain ordering, through WAXS; ii) lamellar crystals arrangement, through SAXS; and iii) amorphous phase evolution through dielectric spectroscopy (DS).

Details relating to the SWD techniques have been reported elsewhere [17]. Simultaneous SAXS, WAXS and DS experiments were performed in the Polymer beam-line at HASYLAB (DESY) [17]. The material used in the present study was a commercial sample of glassy PET (Rhodia S80 from RhodiaSter-Rhone Poulenc, $M_v = 45000$ g/mol) which can be considered as a model polymer to study polymer crystallization [19]. PET, like other glassy polymers, can develop a certain degree of crystallinity provided it is heated at $T > T_g = 75^\circ\text{C}$.

Figure 1 illustrates SAXS-WAXS-DS data during a crystallization experiment at $T_c = 113.5^\circ\text{C}$, taken simultaneously for different crystallization times t_c . The WAXS (a), and SAXS (b) intensities are given as a function of the scattering vector $s = (2/\lambda) \sin \theta$, 2θ being the scattering angle. The SAXS intensities are Lorenz-corrected ($I \cdot s^2$) [23]. The individual contributions for the amorphous halo and for the crystalline peaks (corresponding to the last pattern), used to estimate the crystallinity, are given at the bottom of fig. 1a. Every pattern was recorded with an acquisition time of 1 min. The ϵ'' data from DS are plotted as a function of frequency ($F = \omega/(2\pi)$) ω being the angular frequency. The initial amorphous state, $t_c = 1$ min, is characterized by an amorphous halo in the WAXS pattern, a continuous scattering decreasing with s in the SAXS pattern, due to the liquid-like state, and by the presence of the α relaxation process centered around an F_{\max} value of $4 \cdot 10^5$ Hz in the DS data. As time increases, the onset of crystallization is denoted by the incipient appearance of Bragg peaks in the WAXS patterns characteristic of the 010, $1\bar{1}0$ and 100 reflections of the triclinic unit cell of PET, respectively. In the SAXS pattern an increase of the scattered intensity at lower s -values that develops into a well-defined peak centered around a value of $s = 0.0125 \text{ \AA}^{-1}$ is observed

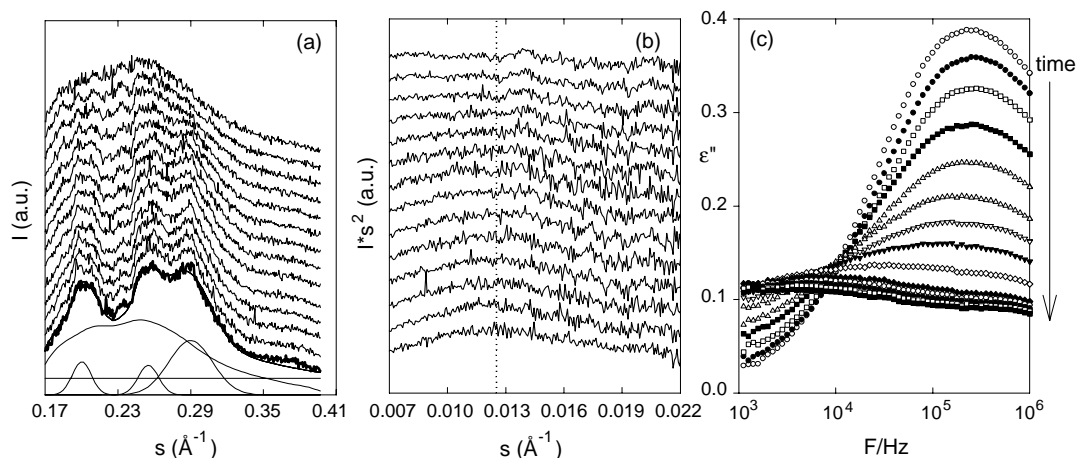


Fig. 1 – Simultaneous WAXS (a), SAXS (b) and DS (c) experiments during crystallization of initially amorphous PET at $T_c = 113.5^\circ\text{C}$. Crystallization time, t_c increases in the direction of the arrow. Time from top to bottom in minutes: 1, 4, 6, 8, 10, 12, 14, 16, 18, 30, 40, 50, 60, 128.

(see dotted line). The above-mentioned structural features are accompanied by the changes in the dynamics of the amorphous phase (see fig. 1(c)). Here, the α relaxation exhibits a decrease of its intensity with crystallization time and a shift towards lower frequencies of F_{\max} . Figure 2 summarizes the changes of the above-mentioned characteristic magnitudes for two different crystallization temperatures. In the upper part of fig. 2 (a and b, respectively), the long-period values (L) calculated from the Lorenz-corrected SAXS intensity, the WAXS crystallinity as estimated from the ratio of the crystalline peak area to the total one (W_c^{WAXS}) [24] and the Lorenz-corrected SAXS intensity (Q) integrated in the measured s -range are presented. In the lower part, the characteristic parameters from the dielectric experiment (F_{\max} and ϵ''_{\max}) are also shown as a function of t_c (fig. 2c and d, respectively). In our analysis of the dielectric data, we do deliberately not attempt any fitting procedure by the Havriliak-Nagami procedure to avoid overinterpretation of our results. As is known, the α relaxation of PET and many other polymers exhibits a high-frequency tail due to the contribution of the β process [4] whose shape cannot be merely extrapolated from low-temperature measurements [25]. As far as the WAXS experiment is concerned (fig. 2(b)), the data follow the characteristic sigmoidal rapid increase of the crystallinity (primary crystallization) followed by a very slow increase for longer times (secondary crystallization) [14]. The crossover times between both processes are characterized by $t_c = 20$ min for $T_c = 113.5^\circ\text{C} \pm 1.5^\circ\text{C}$ and $t_c = 90$ min for $T_c = 105.7^\circ\text{C} \pm 0.5^\circ\text{C}$, respectively. The integrated SAXS intensity, Q , parallels the time-dependence followed by X_c^{WAXS} . It is seen that L only slightly decreases for very short times and remains nearly constant with t_c . The observed behaviour in the primary crystallization regime is consistent with the appearance and growth of semicrystalline spherulitic structures [14,26]. During the secondary-crystallization process the spherulites already fill-in the sample volume [14,26]. The above features provide information about changes occurring in the crystalline phase. With the SWD technique, this structural information can be complemented with that, provided by the DS experiments which are sensitive to changes of the amorphous phase.

Figure 2d shows that the intensity of the α relaxation initially decreases with t_c until about the crossover time is reached and subsequently remains nearly constant. A different behaviour is observed for F_{\max} which slightly varies until the crossover time and subsequently

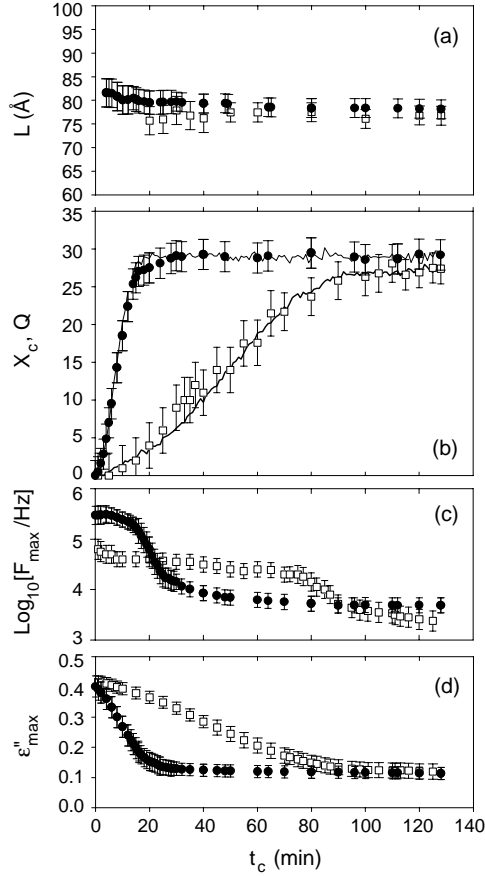


Fig. 2 – Summary of physical parameters obtained from the SWD experiment as a function of crystallization time t_c for $113.5 \pm 1.5^\circ\text{C}$ (●) and $105.7^\circ\text{C} \pm 0.5^\circ\text{C}$ (□). (a) Long spacing L . (b) Crystallinity X_c and SAXS integrated intensity Q (continuous lines). (c) Frequency of maximum loss F_{max} . (d) Maximum loss value ϵ''_{max} . Error bars correspond to average over several experiments.

dramatically decreases reaching a plateau for longer times. From the simultaneous SWD experiments a clear relationship between structure and dynamics emerges as evidenced by the following features: i) For times shorter than the crossover time, the initial strong reduction of the mobile material, reflected by the decrease of ϵ''_{max} , parallels the increase of crystallinity and integrated intensity Q . ii) During primary crystallization, the remaining mobile material does not significantly change the average relaxation time $\langle\tau\rangle$ defined [18] by $\langle\tau\rangle \approx 1/(2\pi F_{\text{max}})$ as reflected by the moderate variation observed in F_{max} . iii) At the crossover time, when primary crystallization finishes, F_{max} exhibits a notable decrease indicating the onset of restrictions in the dynamics of the remaining mobile fraction. The question arises as whether the observed restriction appears as due to a pure geometrical confinement of the amorphous phase [27] or to the formation of incipient secondary crystals producing a pinning of the remaining amorphous phase [28] at the end of the primary-crystallization regime. In the first case, measurements of ethylene glycol confined in cavities of varying size have shown a dramatic increase of the relaxation rate when the size of the cavity is below a certain value [29]. In our case we observe the opposite trend, *i.e.* a slowing-down of the dynamics as crystallinity develops. Recent

experiments performed in systems in which secondary crystallization was strongly hindered either through copolymerization [30,31] or through blending with a non-crystallizable second polymer [32] have shown an invariance in F_{\max} throughout the crystallization process. These findings point to the fact that initial secondary crystals may act as physical cross-links in the amorphous phase slowing down its dynamics.

In summary, the three main features which are directly derived from our simultaneous SAXS, WAXS and DS experiments strongly support the following model for the crystallization process in PET. During primary crystallization, a nanostructure of lamellar stacks develops as detected by the incipient appearance of a long spacing. Although the amount of lamellar stacks increases with time (as revealed by the increase observed in both X_c and Q and the decrease of ϵ''_{\max}) the average distance between the gravity centers of consecutive lamellae within the stacks does not significantly change (constant long spacing). In this regime the average mobility of the remaining mobile amorphous phase is not notably affected, as revealed by the constancy in F_{\max} . Moreover, the invariance of the long spacing and concurrent decrease in F_{\max} upon passing through the crossover time, marking the transition from primary to secondary crystallization, suggests that the restriction to the mobility of the amorphous phase, as revealed by the decrease of F_{\max} , mainly occurs in the inter-lamellar stacks regions and not in the intra-lamellar stacks amorphous regions. We hypothesize that the amorphous regions located between consecutive crystals become strongly arrested in its average mobility as soon as the lamellar stack is formed in the primary crystallization. This would contribute to a modification of the relaxation time distribution function [33] provoking the observed change in the shape of the measured dielectric loss during primary crystallization but not in the experimentally measured F_{\max} values which mainly originate from the inter-lamellar stacks regions. It is at the end of primary crystallization when a strong reduction in the mobility of the amorphous phase is detected, directly probing that further secondary crystals grow under restricted melt conditions as recently suggested [11].

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REFERENCES

- [1] BASSETT D. C., *Principles of Polymer Morphology* (Cambridge University Press, Cambridge) 1981.
- [2] KELLER A., *Philos. Mag.*, **2** (1957) 1171.
- [3] MCCRUM N. G., READ B. and WILLIAMS G., *Anelastic and Dielectrics Effects in Polymeric Solids* (Wiley, New York) 1967.
- [4] BOYD R. H., *Trends Polym. Sci.*, **4** (1996) 12.
- [5] IMAI M., KAJI K. and KANAYA T., *Phys. Rev. Lett.*, **71** (1993) 4162.
- [6] ALBRECHT T. and STROBL G., *Macromolecules*, **29** (1996) 783.
- [7] TERRILL N. J., FAIRCLOUGH P. A., TOWNS-ANDREWS E., KOMANSCHEK B. U., YOUNG R. J. and RYAN A. J., *Polymer*, **39** (1998) 2381.
- [8] WANG Z., HSIAO B., SIROTA E. B., AGARWAL P. and SRINIVAS S., *Macromolecules*, **33** (2000) 978.

- [9] VERMA R., MARAND H. and HSIAO B. S., *Macromolecules*, **29** (1996) 7767.
- [10] NOGALES A., EZQUERRA T. A., BATALLÁN F., FRICK B., LÓPEZ-CABARCOS E. and BALTÁ-CALLEJA F. J., *Macromolecules*, **32** (1999) 2301.
- [11] ALIZADEH A., RICHARDSON L., XU J., MCCARTNEY S., MARAND H., CHEUNG Y. W. and CHUM S., *Macromolecules*, **32** (1999) 6221.
- [12] STROBL G., *Eur. Phys. J. E*, **3** (2000) 165.
- [13] WELCH P. and MUTHUKUMAR M., *Phys. Rev. Lett.*, **87** (2001) 218302.
- [14] ZACHMANN H. G. and WUTZ C., in *Crystallization of Polymers*, edited by DOSIÈRE M. (Kluwer Academic Publishers) 1993.
- [15] WUTZ C., BARK M., CRONAUER J., DÖHRMANN R. and ZACHMANN H. G., *Rev. Sci. Instrum.*, **66** (1995) 1303.
- [16] ECKSTEIN E., QIAN J., THURN-ALBRECHT T., STEFFEN W. and FISCHER E. W., *J. Chem. Phys.*, **113** (2000) 4751.
- [17] ŠICS I., NOGALES A., EZQUERRA T. A., DENCHEV Z., BALTÁ-CALLEJA F. J., MEYER A. and DÖHRMANN R., *Rev. Sci. Instrum.*, **71** (2000) 1733.
- [18] WILLIAMS G., *Adv. Polym. Sci.*, **33** (1979) 59.
- [19] COBURN J. C. and BOYD R. H., *Macromolecules*, **19** (1986) 2238.
- [20] EZQUERRA T. A., MAJSZCZYK J., BALTÁ-CALLEJA F. J., LÓPEZ-CABARCOS E., GARDNER K. H. and HSIAO B. S., *Phys. Rev. B*, **50** (1994) 6023.
- [21] IVANOV D. A., LEGRAS R. and JONAS A. M., *Macromolecules*, **32** (1999) 1582.
- [22] FUKAO K. and MIYAMOTO Y., *Phys. Rev. Lett.*, **79** (1997) 4613.
- [23] BALTÁ-CALLEJA F. J. and VONK C. G., *X-ray Scattering of Synthetic Polymers* (Elsevier, Amsterdam) 1989.
- [24] BLUNDELL D. J. and OSBORN B. N., *Polymer*, **24** (1983) 953.
- [25] CASALINI R., FIORETTO D., LIVI A., LUCCHESI M. and ROLLA P. A., *Phys. Rev. B*, **56** (1997) 3016.
- [26] SCHULTZ J. M., *Polymer Material Science* (Prentice Hall, New York) 1974.
- [27] SCHICK C. and DONTH E., *Phys. Scr.*, **43** (1991) 423.
- [28] ROLAND C. M., *Macromolecules*, **27** (1994) 4242.
- [29] HUWE A., KREMER F., BEHRENS P. and SCHWIEGER W., *Phys. Rev. Lett.*, **82** (1999) 2338.
- [30] NOGALES A., EZQUERRA T. A., GARCÍA J. M. and BALTÁ-CALLEJA F. J., *J. Polym. Sci. B*, **37** (1999) 37.
- [31] ŠICS I., EZQUERRA T. A., NOGALES A., BALTÁ-CALLEJA F. J., KALNINS M. and TUPUREINA V., *Biomacromolecules*, **2** (2001) 581.
- [32] SY J. W. and MIJOVIC J., *Macromolecules*, **33** (2000) 933.
- [33] SCHLOSSER E. and SCHOENHALS A., *Colloid Polym. Sci.*, **267** (1989) 963.