Influence of microstructure on the crystallization of segmented copolymers constituted by glycolide and trimethylene carbonate units

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Abstract. Hot and cold non-isothermal crystallization of copolymers having glycolide hard segments and glycolide-co-trimethylene carbonate soft segments was investigated by calorimetry, optical microscopy and synchrotron radiation experiments. The effect of composition and microstructural changes on thermal properties and morphology of crystallized samples was analyzed. Significant differences were found between the nucleation density of spherulites developed during cold crystallization. Crystallizations from the melt were characterized by a lamellar insertion mechanism and a broad distribution of crystal layer widths. By contrast, cold crystallized samples gave rise to practically constant long periods and narrower distributions. Soft segments with high glycolide content were more easily incorporated in the crystalline phase by decreasing the hard segment content of the sample. A significant decrease on the melting point was observed as well as a decrease of the amorphous layer thickness and an increase of the crystalline lamellar thickness when the sample was hot and cold crystallized, respectively.

Keywords: biodegradable polymers, polyglycolide, surgical sutures, polymer crystallization, synchrotron radiation

1. Introduction

Segmented copolymers are an interesting class of thermoplastic materials because mechanical properties similar to those of cross-linked elastomers can be achieved. Basically, copolymers are formed by the combination of a ‘soft’ block comprising units with a random distribution that gives rise to an amorphous phase with a low \( T_g \) and a ‘hard’ block comprising units which can crystallize to form rigid physical crosslinks. Properties are highly dependent on the phase separation induced by crystallization and on the structure of the crystalline phase. In general, reduced hard segment content hinders crystallization and leads to a decrease in the melting temperature.

Typically, hard blocks in segmented copolymers are polyurethanes, poly(butylene terephthalate) or poly-amides, with polyethers or aliphatic polyesters acting as the soft blocks [1–4]. Polyurethanes have been intensively studied for several decades, mainly as tissue engineering scaffolds and vascular implants because of their compatibility, elasticity and ease of surface modification.

The use of several soft segments to achieve effective elastomeric and biocompatible properties is being investigated. Specifically, soft segments constituted by trimethylene carbonate units are gaining acceptance over more traditional ones based on diisocyanate units due to potential toxicity concerns regarding degradation products of the latter [6–8]. Segmented polymers also play a fundamental role in the development of bioabsorbable monofilament surgical sutures. These sutures have clear advantages over conventional braided sutures (e.g. polyg-
lycolide) since they are more resistant to harbor microorganisms and exhibit less resistance to passage through tissue. However, these materials must meet strict requirements concerning mechanical properties (e.g. high flexibility and adequate tensile strength), which can only be achieved by employing copolymers with some elastomeric characteristics. Thus, commercial monofilament sutures are mainly constituted by hard segments based on polyglycolide and soft segments based on trimethylene carbonate, \(\varepsilon\)-caprolactone and/or \(p\)-dioxanone units (e.g. Maxon\textsuperscript{TM} with glycolide and trimethylene carbonate \[9\], Monosyn\textsuperscript{TM} with glycolide, \(\varepsilon\)-caprolactone and trimethylene carbonate \[10\], and Biosyn\textsuperscript{TM} with glycolide, \(p\)-dioxane and trimethylene carbonate) \[11\]. The main goal of the present work concerns to the study of biodegradable segmented copolymers constituted by polyglycolide (PGL) hard segments and poly(glycolide-co-trimethylene carbonate) soft segments. The influence of the hard segment content and composition of the soft segment on the crystallization process will be considered since properties and degradability strongly depend on final morphology and crystallinity.

Phase separation, crystalline morphology and crystallization kinetics of simple block copolymers have been widely studied experimentally as well as theoretically \[12\–16\]. Thus, microstructures that can form from the melt, from solution and for both thin and bulk samples have been extensively reviewed \[17, 18\], and even some works focus on the production of single crystals of diblock copolymers \[19, 20\]. By contrast, little research is available on the crystallization behavior of segmented copolymers mainly due to the complexity of their structure \[21\]. On the other hand, it is well known that polymer morphology has a strong influence on properties and also on degradation mechanisms when samples have bonds susceptible to hydrolytic or enzymatic attack.

Taking into account that polymers are usually processed under non-isothermal conditions, it is also highly important the get insight the understanding of the development of crystal morphology and crystallinity during the non-isothermal crystallization of the proposed segmented copolymers.

2. Experimental section

2.1. Materials

Synthesis of segmented copolymers constituted by glycolide and trimethylene carbonate followed a two-step strategy by which first a soft segment with a theoretically random distribution was prepared by reaction of the two monomers using a difunctional initiator (e.g. diethylenglycol). Then, two hard segments were incorporated at each end of the middle soft segment by subsequent postpolymerization of glycolide (Figure 1). A triblock copolymer was also obtained from a soft segment constituted by trimethylene carbonate only. Synthesis, characterization and evaluation of the basic properties of these samples had previously been performed \[22\]. Relevant data concerning the samples used in this work are summarized in Table 1. All copolymers are hereafter named as GL-\(b\)-[TMC-co-GL]-\(b\)-GL \(x\–z\), where \(x\) and \(z\) refer to TMC weight percentage in the soft segment and in the final product, respec-

![Figure 1. Schemes showing the two-step synthesis of GL-\(b\)-[TMC-co-GL]-\(b\)-GL \(x\–z\) copolymers (a) and the expected microstructure of the studied samples (b)](image)

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tively. According to this notation, \( x = 100 \) corresponds to a triblock copolymer and \( x = z \) to a random copolymer. The trimethylene carbonate content of the soft segment and the final copolymer allowed the estimation of the weight percentage of hard polyglycolide segments (\( HS \)), given by Equation (1), also summarized in Table 1:

\[
HS \text{ [wt %]} = 100 \left( 1 - \frac{z}{x} \right)
\]  

(1)

2.2. Measurements

Calorimetric data were obtained by differential scanning calorimetry with a TA Instruments Q100 series equipped with a refrigerated cooling system (RCS) operating from \(-90 \) to \( 550 \) °C. Experiments were conducted under a flow of dry nitrogen with a sample weight of approximately \( 10 \) mg while calibration was performed with indium. Cooling and heating runs were performed at a rate of \( 3 \) °C/min from the melt and glass state, respectively. The latter were carried out by cooling a previously melted sample at the maximum rate allowed by the RCS equipment.

Spherulitic morphologies were studied using a Zeiss Axioskop 40 Pol light polarizing microscope equipped with a Linkam temperature control system configured by a THMS 600 heating and freezing stage connected to an LNP 94 liquid nitrogen cooling system. Micrographs were taken with a Zeiss AxiosCam MRC5 digital camera. A first-order red tint plate was employed to determine the sign of spherulite birefringence under crossed polarizers. Spherulites were grown from homogeneous melt-crystallized thin films obtained by melting \( 1 \) mg of the polymer over microscope slides. Next, small sections of these films were pressed or smeared between two cover slides and inserted into the hot stage. The thickness of the squeezed samples was in all cases close to \( 10 \) µm. Samples were maintained at approximately \( 10 \) °C above the polymer melting point for \( 5 \) minutes to wipe out sample thermal history effects. For hot crystallization experiments, samples were rapidly cooled to a selected temperature, isothermally maintained at this temperature for \( 3 \) minutes for equilibration and then cooled at \( 3 \) °C/min. Optical microscopy observations revealed that no spherulites formed at the end of this isothermal step. For cold crystallization experiments, the above melted samples were quenched in liquid nitrogen and then heated to the selected crystallization temperature at a rate of \( 3 \) °C/min.

Simultaneous time-resolved SAXS/WAXD experiments were carried out at the CRG beamline (BM16) of the European Synchrotron Radiation Facility of Grenoble. The beam was monochromatized to a wavelength of \( 0.098 \) nm. Polymer samples were confined between Kapton films and then held on a Linkam hot stage with temperature control within \( \pm 0.1 \) °C. WAXD profiles were acquired during heating and cooling runs in time frames of \( 12 \) s and at rates of \( 3 \) °C/min. Two linear position-sensitive detectors were used [23]: the SAXS detector was calibrated with different orders of diffraction from silver behenate whereas the WAXD detector was calibrated with diffractions of a standard of an alumina (\( \text{Al}_2\text{O}_3 \)) sample. The diffraction profiles were normalized to the beam intensity and corrected considering the empty sample background. WAXD peaks were deconvoluted with the PeakFit v4 program by Jandel Scientific Software using a mathematical function known as ‘Gaussian and Lorentzian area’ (Pearson VII function). The correlation function and corresponding parameters were calculated with the CORFUNC program [24] for Fiber Diffraction/Non-Crystalline Diffraction, CCP13, provided by the Collaborative Computational Project 13.

3. Results and discussion

3.1. Thermal behavior

Figures 2 and 3 compare the cooling and heating runs from the melt and the glass state, respectively,
of all synthesized samples. Changes in the hot crystallization behavior and thermal properties of melt quenched samples (glass transition temperature, cold crystallization and melting peaks) were clearly observed (Table 1). Thermal history of the as synthesized samples was erased by a former heating run and consequently the reported calorimetric data correspond to samples processed in a similar way. The following observations can be made:

1. Hot crystallization peaks clearly shifted towards lower temperatures for lower HS contents (Figure 2 and Table 1). The influence of the HS content is noticeable since a decrease from 67.5 to 50% led to a shift of the crystallization peak from 184 to 140°C, respectively. Comparison between samples with the same HS content (i.e. GL-b-[TMC-co-GL]-b-GL 60–23 and GL-b-[TMC-co-GL]-b-GL 85–32.5 samples) revealed a slightly lower crystallization peak temperature for the sample with a lower glycolide content in its soft segment (i.e. 164°C, as against 170°C). Hence, crystallization is clearly favored by the increase of the hard segment content and even when the glycolide content of the soft segment is sufficient to allow its incorporation into the crystalline phase. Crystallization enthalpy data (Table 1) are also in full agreement with this conclusion.

2. The glass transition temperatures of segmented samples having the same trimethylene carbonate content (i.e. GL-b-[TMC-co-GL]-b-GL 85–32.5 and GL-b-[TMC-co-GL]-b-GL 65–32.5) were similar and slightly lower than that of PGL due to their relatively low TMC content (32.5 wt%). This temperature logically increased (from 16.0–18.5 to 21.4°C) with decreasing the TMC content (i.e. from 32.5 to 23 wt%). In any case, it is worth emphasizing that all segmented copolymers had a completely miscible amorphous phase from which crystallization occurred during the subsequent heating process. Note that it was not possible to get completely amorphous samples at the maximum cooling rate allowed by the equipment since the enthalpy of the cold crystallization peak was always lower than the melting enthalpy. Thus, the amorphous phase should have a higher TMC content than expected from the copolymer composition and consequently cautions must be taken into account when $T_g$ is correlated with composition. Logically, the block copolymer GL-b-[TMC-co-GL]-b-GL 100–32.5 had a significantly lower glass transition temperature since its soft segment was only constituted by trimethylene carbonate units.

3. Cold crystallization peaks appeared in a narrow temperature range (74–82°C) but slight differences in temperature and enthalpy were detected. These differences were in full agreement with the expected difficulty to crystallize when the...
HS segment content decreased (i.e. the highest temperature and the lowest enthalpy corresponded to GL-b-[TMC-co-GL]-b-GL 65–32.5 sample).

4. Melting temperatures and enthalpies of the synthesized samples increased with HS content, indicating the formation of more perfect domains. Interestingly, the melting temperatures of the two samples with the same HS content (i.e. GL-b-[TMC-co-GL]-b-GL 60–23 and GL-b-[TMC-co-GL]-b-GL 85–32.5) were significantly different, and specifically a higher value was found when the soft segment was enriched on TMC units. The decrease in the melting temperature was associated with the incorporation of foreign units in the crystalline phase, which should be greater (in agreement with the experimental observation) when the soft segment was able to be incorporated into the crystalline phase due to its higher glycolide content. However, differences in lamellar thickness could also play an important role, and consequently synchrotron experiments appear to be a useful tool to understand the behavior observed.

3.2. Optical microscopy observations on the spherulitic morphologies of hot and cold crystallized samples

Spherulites obtained at the end of cold and hot non-isothermal crystallizations had always a positive birefringence and a fibrilar texture as shown in Figure 4. Spherulites observed in a determined cold crystallization experiment had a similar size, whereas a slightly greater variability (Figure 4d) was detected in the fewer spherulites that formed in the hot crystallized samples. Differences can mainly be attributed to an impingement effect instead of a thermal nucleation where nuclei became progressively active during the cooling rate. Nucleation density of the studied thin films was in general low and high for hot and cold crystallized samples, respectively (Table 2, Figure 4). It is worth

![Figure 4. Spherulitic morphologies of GL-b-[TMC-co-GL]-b-GL x–z copolymers after being cold (a,b,c) and hot crystallized (d, e, f) at a rate of 3°C/min from the glass and the melt state, respectively. Insets show details of micrographs taken using a first-order red tint plate](image-url)
pointing out that clear differences were detected among the cold crystallized samples (Figures 4a, 4b and 4c) and consequently physical properties of the studied copolymers should be distinct when processed from the glass state.

It is remarkable that GL-\textit{b-[TMC-co-GL]}-\textit{b-GL} 60–23 had a considerable lower nucleation density than GL-\textit{b-[TMC-co-GL]}-\textit{b-GL} 85–32.5, although both samples had the same \textit{HS} content. In fact, spherulites of the two samples at the end of crystallization had highly different diameter sizes (i.e. close to 55 and 12 µm). Crystallization may be disfavoured when the copolymer had TMC rich soft segments (e.g. \textit{x-z} = 85–32.5) since they were not able to be incorporated in the crystalline structure, and hindered the proper arrangement of hard blocks. Note that soft and hard segments were initially well mixed as a consequence of their partial affinity and the spatial restrictions imposed by chemical linkages. Molecular transport plays a highly important role in low temperature cold crystallization and consequently the diffusion of soft segments far away from the crystal growth surface should be difficult. Crystallization proceeded in this case through the formation of a great number of primary nuclei.

Crystal growth rates (\textit{G}) can be determined from non-isothermal cold crystallization experiments by measuring the change on the spherulitic radius (\textit{R}) with temperature (\textit{T}) during heating runs performed at a constant rate (d\textit{T}/d\textit{t}). The plot of the radius versus temperature allows the calculation of its first derivative (d\textit{R}/d\textit{T}) at each temperature and the corresponding \textit{G} value [25, 26], as given by Equation (2):

\[
\text{\textit{G} = \frac{d\textit{R}}{d\textit{t}} = \left(\frac{d\textit{R}}{dT}\right)\left(\frac{dT}{dt}\right)}
\]

Figure 5 shows the evolution of the spherulitic radius and the crystal growth rate of the three segmented copolymers studied in this work when they were cold crystallized at a heating rate of 3°C/min. The high nucleation of GL-\textit{b-[TMC-co-GL]}-\textit{b-GL} 85–32.5 forced that its crystallization data were restricted to a short temperature interval whereas the other samples covered a higher temperature range since spherulites were able to grow to larger dimensions. It is clear that the estimated data corresponded to the left side of typically bell shaped curves and that the average crystal growth rate decreased in the order of \textit{x-z} values: 85–32.5 > 60–23 > 65–32.5 (i.e. the lowest rate corresponded to the sample with the lowest polyglycolide hard content).

Spherulites coming from hot crystallization experiments had remarkably bigger diameter sizes (i.e. from 200 to 250 µm) than those above discussed, but in this case scarce differences were found between the different copolymers. Hence, variations on the overall crystallization rates were mainly a consequence of the differences between the crystal growth rates which in this case were mainly influenced by the secondary nucleation constant. Lamellae of copolymers having higher \textit{HS} content had more favourable surfaces to induce secondary nucleation and showed the higher crystallization rates.

Well differentiated amorphous domains should always develop, as will be below explained from the analysis of synchrotron experiments. These domains were probably formed inside the spherulites and affected their optical properties. Note that chain connectivity should lead to crystalline PGL hard segments and amorphous TMC rich soft segments occupying the same spherulite. Black irregular zones in the birefringent spherulite arms (e.g. dashed circle in Figures 4d–4f where big spherulites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nucleation density [Nuclei/mm²]</th>
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<tr>
<td></td>
<td>Hot crystallization</td>
</tr>
<tr>
<td>85</td>
<td>32.5</td>
</tr>
<tr>
<td>65</td>
<td>32.5</td>
</tr>
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<td>60</td>
<td>23</td>
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Figure 5. Evolution of the spherulitic radius (full symbols) and the crystal growth rate (empty symbols) during non-isothermal crystallization of GL-\textit{b-[TMC-co-GL]}-\textit{b-GL} 85–32.5 (●), GL-\textit{b-[TMC-co-GL]}-\textit{b-GL} 65–32.5 (▲) and GL-\textit{b-[TMC-co-GL]}-\textit{b-GL} 60–23 (●) samples.
are depicted) appeared and gave rise to a speckled appearance that can be clearly distinguished from usual ringed textures developed at high temperatures. Although, the spherulitic morphology depends on the crystallization temperature, it should be indicated that the indicated irregular textures were always observed independently of the polymer sample and even on the experimental crystallization conditions.

3.3. Study on the non-isothermal hot crystallization of GL-b-(TMC-co-GL)-b-GL samples by time-resolved SAXS/WAXD experiments

Figure 6a shows time-resolved SAXS profiles of the representative GL-b-(TMC-co-GL)-b-GL 85–32.5 sample obtained during a non-isothermal hot crystallization performed at a rate of 3°C/min. A SAXS long period peak is clearly seen at a value of the scattering vector \( q = \frac{4\pi/\lambda}{\sin(\theta)} \) in the 0.39–0.31 nm\(^{-1}\) range after subtraction of the empty sample background observed near the beam stop. This peak can be attributed to the lamellar structure of spherulites and started to appear at a temperature which in general decreased with reducing the HS content of the sample. Next, the peak intensity increased significantly with decreasing temperature until reaching a maximum value since a small decrease was subsequently detected. In any case, the SAXS peak reached high intensity, as expected for a large difference in electronic density of the amorphous and the crystalline phases. In fact, polyglycolide crystallizes according to a very tight packing that is peculiar with respect to other aliphatic polyesters [27, 28].

SAXS data were quantitatively analyzed by the normalized one-dimensional correlation function [29], \( \gamma(r) \), which corresponds to the Fourier transform of the Lorentz-corrected SAXS profile, as shown by Equation (3):

\[
\gamma(r) = \frac{\int_0^\infty q^2 I(q) \cos(qr) dq}{\int_0^\infty q^2 I(q) dq}
\]  

(3)

The scattering intensity was extrapolated to both low and high \( q \) values using Vonk’s model [30] and Porod’s law, respectively. Correlation functions were used to determine the evolution during crystallization of the scattering invariant, \( Q \), associated with the peak intensity and morphological parameters like the long period, \( L_c \), crystalline lamellar thickness, \( l_c \), and amorphous layer thickness, \( l_a \).

Figure 6b compares the evolution of the scattering invariant, \( Q \), with the temperature for all samples. The resemblance between the scattering invariant profiles of the two samples with the same HS content (i.e. the maximum value of the invariant was reached at a relatively similar temperature) is worth noting, although the induction time and the slope of the invariant plot were slightly longer and lower, respectively, for the GL-b-[TMC-co-GL]-b-GL 85–32.5 sample. DSC data (Figure 2) also revealed that the hot crystallization peak of this sample was slightly wider and started to appear at a lower tem-

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**Figure 6.** a) Time-resolved SAXS three-dimensional profiles of the GL-b-[TMC-co-GL]-b-GL 85–32.5 sample during the hot crystallization performed at a cooling rate of 3°C/min. b) Plot of the intensity of the SAXS reflection during cooling for the three studied segmented copolymers.
perature. Logically, the sample with the lowest HS content (i.e. GL-b-[TMC-co-GL]-b-GL 65–32.5) had the highest induction time and the corresponding invariant increased at the slowest rate, especially during the first crystallization steps. The final decrease in the SAXS peak intensity, which was always detected, suggests a change in the amorphous phase since this value depends on the degree of crystallinity but also on the difference between the electronic densities of amorphous and crystalline phases. It is clear that on cooling the amorphous interlamellar component should adopt a more compact molecular arrangement.

Time-resolved WAXD profiles of the representative GL-b-[TMC-co-GL]-b-GL 85–32.5 sample obtained during the non-isothermal hot crystallization process can be seen in Figure 7. The initial WAXD profiles show two amorphous halos (inset) whose intensity decreases with crystallization and on which Bragg reflections form. Those most intense appear at 0.400 nm \( (q = 15.70 \text{ nm}^{-1}) \) and 0.310 nm \( (q = 20.26 \text{ nm}^{-1}) \) and can be indexed as the (110) and (020) reflections of the polyglycolide structure, defined by an orthorhombic unit cell having \( a = 0.522 \text{ nm} \), \( b = 0.619 \text{ nm} \) and \( c \) (chain axis) = 0.702 nm [28]. The intensities of these reflections increased significantly at the beginning of crystallization and subsequently at a moderate rate (which should be associated with the secondary crystallization) until reaching an asymptotic value (see dashed lines in Figure 7). The SAXS long period peak and crystal diffractions appeared simultaneously for all samples, as expected for a crystallization process controlled by nucleation and crystal growth. The evolution of the mass fraction of the crystalline phase in the sample, \( X_c^{\text{WAXD}} \), was determined from the deconvoluted WAXD profiles as the ratio between the total intensities of the crystalline reflections \( I_c \) and the overall intensity \( I_T \). Values at the end of crystallization ranged between 0.38 and 0.44 depending on the copolymer microstructure and were ordered in complete agreement with DSC observations (i.e. the highest and lowest crystallinities corresponded to samples with \( x-y \) values of 60–23 and 65–32.5, respectively).

Figure 8 plots the values of morphological parameters, scattering invariant and the calculated degree of crystallinity in function of the temperature during the cooling run performed at 3ºC/min for GL-b-[TMC-co-GL]-b-GL 85–32.5 as a representative copolymer. A remarkable change in the long period (e.g. from 19.0 to 15.7 nm for the above sample) was detected for the three copolymers. This decrease was mainly due to the contribution of the crystalline lamellar thickness, which diminished in a similar ratio (i.e. from 15.5 to 12.5 nm). This is commonly observed when a lamellar insertion mechanism occurs because of spatial restrictions caused by the thicker lamellae that first crystallize at higher temperatures. As crystallization proceeds, new lamellae should form in the loosely stacked bundles of primary lamellae, leading to thinner defective crystals. Figure 8 also shows that the amorphous layer thick-

![Figure 7](image7.png)  
**Figure 7.** Time-resolved WAXD three-dimensional profiles of the GL-b-[TMC-co-GL]-b-GL 85–32.5 sample during the hot crystallization performed at a cooling rate of 3ºC/min. Inset shows the deconvolution of the X-ray profiles taken at room temperature.

![Figure 8](image8.png)  
**Figure 8.** Temperature evolution of the long period, \( L_v \), crystal thickness, \( l_c \), amorphous thickness, \( l_a \), scattering invariant, \( Q \), and degree of crystallinity \( X_c^{\text{WAXD}} \) during a non-isothermal hot crystallization of the GL-b-[TMC-co-GL]-b-GL 85–32.5 sample performed at a cooling rate of 3ºC/min.
ness remained practically constant except at the early stages of crystallization, where a slight decrease probably caused by an improved arrangement of the folding surfaces was observed. In fact, the maximum value of the invariant was reached and the main morphological changes had already taken place at the end of the primary crystallization (i.e. spacings remained practically constant or decreased very slightly during the secondary crystallization).

The amorphous and crystalline thicknesses evolved very similarly for the three samples (Figure 9) if the temperature shift associated with the hindered crystallization of the copolymer with the lowest HS content (i.e. GL-b-[TMC-co-GL]-b-GL 65–32.5) is considered. Note that all samples had very similar l_c values at the beginning (16–15.2 nm) and even at the end of the crystallization process. This suggests that some TMC units were able to be incorporated into the crystalline lamellar regions, resulting in a clear decrease in amorphous lamellar thickness (Figure 9).

The assignment of l_a and l_c thicknesses was verified from the combined SAXS and WAXD data as it is well known that they could not be distinguished from the analysis of the correlation function [31, 32]. Thus, the ratio between X_cWAXD and X_cSAXS (determined as l_c/(l_c + l_a)) is an estimate of the volume-filling fraction of the lamellar stacks, X_S, which should be lower than 1 for a correct assignment. This value ranged between 0.55 and 0.42 for the three copolymers and the given assignment. The lowest volume-filling fraction corresponded to the GL-b-[TMC-co-GL]-b-GL 65–32.5 sample since amorphous phase domains between lamellar stacks were more significant in the samples with a lower HS content.

Large discrepancies between SAXS and WAXD crystallinities are common in the literature [33] and have been explained by the assumption of the existence of amorphous phase domains. Note also that the given assignment led to a crystalline lamellar thickness, l_c, close to 12 nm, which is a rather typical value of polyester single crystals [34–36]. Moreover, a lamellar thickness of only 2.5–3.2 nm is difficult to combine with the hkl reflections detected in the X-ray diffraction patterns due to the expected reduced number of chain repeat units within the lamellae (i.e. lamellar thickness should correspond to four units only). Similarities in crystalline lamellar thicknesses attained for all samples clearly indicate that differences in melting points must be attributed to the incorporation of foreign trimethylene carbonate units into polyglycolide crystals rather than to the existence of lamellar crystals with different thicknesses. Specifically, the high melting point decrease observed for GL-b-[TMC-co-GL]-b-GL 65–32.5 (i.e. more than 20°C with respect to the GL-b-[TMC-co-GL]-b-GL 100–32.5 copolymer was determined in the heating runs performed at 20°C/min with the hot crystallized samples) is only due to the ability of soft segments to become incorporated into the crystalline phase.

Figure 10 compares the correlation functions achieved at room temperature with the three segmented copolymers, including that corresponding to the triblock sample for completeness. It is clear that the most different function was obtained with the GL-b-[TMC-co-GL]-b-GL 65–32.5 copolymer as clearly lower values were reached for the extrapolated l_a value and the spacings associated with the first minimum and maximum of the function. The L_a value associated with the most probable distance between the centers of gravity of two adjacent crystals (abscise of the first maximum of the correlation function) is generally greater than the long period determined from twice the abscise value of...
the first minimum of the correlation function, which is interpreted as the most probable distance between the centers of gravity of a crystal and its adjacent amorphous layer. This indicates a broader distribution of the layer widths of the major component [33], which corresponds to the crystal phase. This broadness is clearly higher for the GL-b-[TMC-co-GL]-b-GL 65–32.5 copolymer (i.e. 5.70 and 14.05 nm were determined, as it can be seen in Figure 10), which exhibited the greatest variation in crystalline lamellar thickness during crystallization, and consequently the largest insertion mechanism. Figure 10 also shows that the maximum and minimum of the correlation function were slightly better defined for the copolymer with the highest glycolide content (GL-b-[TMC-co-GL]-b-GL 60–23), suggesting a larger difference in the electronic densities of its amorphous and crystalline phases.

3.4. Study on the non-isothermal cold crystallization of GL-b-(GL-co-TMC)-b-GL samples by time-resolved SAXS/WAXD experiments

SAXS and WAXD profiles taken during cold crystallization of the representative GL-b-[TMC-co-GL]-b-GL 60–23 sample are illustrated in Figure 11. It can be seen that SAXS and WAXD peaks started to appear at practically the same temperature and that intensity increased significantly in the range of a few degrees. The secondary crystallization was slower and involved a larger temperature interval.

The SAXS peak always increased during crystallization since the effect of densification of the amorphous phase was not produced. Note that the temperature increased during cold crystallization, leading to an expansion of the amorphous phase. The correlation functions corresponding to the SAXS profile of maximum intensity during hot crystallization and at the end of cold crystallization of the GL-b-[TMC-co-GL]-b-GL 60–23 sample are compared in Figure 12. It is clear that lamellae developed with a smaller thickness and a narrower width distribution during cold crystallization (the distance of the first maximum was practically twice that

Figure 10. Correlation functions corresponding to the room temperature SAXS profile during cooling runs (3ºC/min) of the triblock and the three studied segmented copolymers.
associated with the first minimum). In addition, minima and maxima were better defined in the correlation function corresponding to the cold crystallized sample, suggesting a larger difference in the electronic densities of amorphous and crystalline phases. The evolution of crystalline parameters, invariant and crystallinity are compared in Figure 13 for the two segmented copolymers with different HS content and composition. Both samples showed a rapid and very slow increase in the degree of crystallinity during primary and secondary crystallization, respectively. Final values were logically higher for the sample with higher hard segment content (i.e. 38%, as against 35%) and lower than those obtained after hot crystallization (i.e. 44%, as against 38% for the GL-b-[TMC-co-GL]-b-GL 65-32.5 sample).

Amorphous layer thickness remained practically constant during cold crystallization, was similar for the two samples and significantly lower than that deduced for the hot crystallized samples (i.e. 2.1–2.2 nm, as against 2.45–3.08 nm). The main distinctive feature between the two cold crystallized samples was the crystalline lamellar thickness, which was significantly higher for the sample with lower polyglycolide hard segment content. Once again, it seems that soft segments were able to be incorporated into the crystal phase, giving rise to more imperfect crystals and a lower melting point (i.e. 194°C, as against 212°C, as indicated in Table 1). Higher segregation of trimethylene carbonate rich sequences was consequently favored for samples with a higher glycolide content and consequently a lower crystalline thickness was attained. In this case, this thickness remained practically constant during crystallization in contrast with the moderate thickening process detected for the second sample (i.e. from 9.7 to 11.5 nm). Calculated SAXS crystallinities were identical than those determined at the end of hot crystallization (i.e. 83 and 79% for the samples with the low and high HS content, respectively), but obviously the amorphous phase domains between lamellar stacks were more significant in the cold crystallized samples. Thus, the volume-filling fraction decreased up to 0.42–0.48, the lowest value corresponding again to the sample with the lower HS content.

4. Conclusions
Small changes in composition (e.g. from 23 to 32.5 wt% of trimethylene carbonate units) and microstructure (e.g. hard segment content ranging from 50 to 67.5%) of segmented glycolide/trimethylene carbonate copolymers had a great influence on thermal properties, crystallization behavior and morphology of both spherulites and constitutive lamellae. Spherulites were clearly different for cold crystallized samples; specifically, the highest nucleation rate and the lowest crystal growth rate were characteristic of copolymers having high and low hard segment contents, respectively. Crystallization from the melt was characterized by a lamellar insertion mechanism whereas lamellar thickness remained practically constant or even increased slightly during cold crystallization. Amorphous phase domains were remarkable between

Figure 13. Temperature evolution of the long period, \( L_c \), crystal thickness, \( l_c \), amorphous thickness, \( l_a \), scattering invariant, \( Q \), and degree of crystallinity \( X_{WAXD} \), during a non-isothermal cold crystallization of the GL-b-[TMC-co-GL]-b-GL 65–32.5 (a) and GL-b-[TMC-co-GL]-b-GL 60–23 (b) samples performed at a cooling rate of 3°C/min.
lamellar stacks and became more significant for cold crystallized samples. The sample having the lowest hard segment content and a soft segment with a significant glycolide content gave rise to the lowest volume-filling fraction, the most imperfect crystals and the lowest melting temperature. In this case, some trimethylene carbonate units of the soft segment were able to be incorporated into the crystal phase, leading to the highest SAXS crystallinity. Specifically, the highest crystal lamellar thickness and the lowest amorphous layer thickness were attained for cold and hot crystallized samples, respectively. Furthermore, these samples had the broadest lamellar width distribution.

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