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Molecular Weight and Crystallization Temperature Effects on Poly(ethylene terephthalate) (PET) Homopolymers, an Isothermal Crystallization Analysis

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Abstract: The isothermal crystallization of poly(ethylene terephthalate) (PET) homopolymers with different molecular weight was studied in a wide temperature range (140–230 °C) using different experimental techniques. Three different morphological regions, labeled r_1 , r_2 and r_3 , were distinguished as a function of crystallization temperature (T_c). In r_1 (low T_c) crystallized samples were characterized by a low crystalline degree with a small spherulite texture containing thin crystals. In r_2 (intermediate T_c) samples showed medium size spherulites composed of two distinct crystalline families (thin and thick crystals). In this temperature range, the crystallization exhibited a maximum value and it was associated with a high content of secondary crystals. In r_3 (high T_c), samples presented considerable amorphous zones and regions consisting of oversized spherulites containing only thick crystals. Time-resolved wide-angle X-ray diffraction measurements, using synchrotron radiation, indicated a rapid evolution of the crystalline degree within the second region, in

contrast with the quite slow evolution observed in the third region. On the other hand, by small-angle X-ray scattering (SAXS) and time-resolved SAXS experiment, it was found that the long period (L) as well as the lamellar thickness (l_c) increase as a function of T_c , corroborating the formation of the thickest crystals in the third region. From all these observations, a morphological model was proposed for each region.

Keywords: isothermal crystallization; PET; secondary crystallization; synchrotron radiation

1. Introduction

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic of high commercial interest. Due to its good physical and chemical properties, this polymer is used a lot in the manufacture of fibers and films. Also, an important amount of this polymer is used for the fabrication of bottles for a variety of beverages [1]. As a semicrystalline polymer, PET has been studied in both isothermal and dynamical crystallization regimes [2,3]. Variables affecting the crystallization process are molecular weight, crystallization temperature, co-monomer content, nucleating agents, among others [4]. Of particular interest is the effect of both molecular weight and crystallization temperature because small variations in these parameters can produce significant changes in morphology and properties. For instance, under isothermal conditions, the spherulite growth rate decreases significantly with increasing the molecular weight, while the maximum spherulite radius is obtained at the highest crystallization temperature [4]. The latter effect is much more pronounced in PETs of low molecular weight. In addition, the amount of secondary crystals increases with increases in this molecular parameter [5]. On the other hand, it was reported that crystallinity as well as lamellar thickness and crystal perfection increase as a function of T_c for samples exposed to long crystallization times (17 h) [6,7]. At high T_c , perfect crystals are normally obtained, while at low T_c , perfect and imperfect crystals are formed. Perfect crystals are in fact dominant lamellae inside spherulites, while imperfect crystals are subsidiary lamellae [8]. This phenomenon has been previously proposed in terms of crystal growth regimes, where at high T_c , a smooth crystal surface is obtained, while highly imperfect crystals are obtained at low T_c , and an intermediate where nucleation and growth or diffusion rates are comparable [9]. In spite of the great number of studies on the isothermal crystallization of PET [1–8], few reports analyze simultaneously the effect of molecular weight and degree of supercooling on the crystallization process of this polymer. The present work aims to provide, via utilization of conventional and advanced techniques, a more complete analysis of the isothermal crystallization of PET by taking into account the simultaneous effects of both the molecular weight of the material, as well as the degree of supercooling in the polymer crystallization process.

2. Experimental Section

2.1. Materials

PET samples were kindly supplied by Eastman Chemical Co. (Kingsport, TN, USA), Voridian (Voridian de Mexico, S.A. de C.V., Mexico) and AKRA (Fibras Químicas, Monterrey, Mexico).

Weight-average molecular weights (M_w) of samples were 55,200 and 72,521 $\text{g}\cdot\text{mol}^{-1}$, and M_w/M_n were 2.57 and 2.1, respectively. For these samples, no additives were used. For sake of brevity these samples were codified as PET-LMw and PET-HMw, respectively. All samples were dried in a vacuum oven for 6 h at 60 °C before use.

2.2. Polarizing Optical Microscopy (POM)

Sequential micrographs were obtained along the crystallization process in an Olympus BX60 polarizing optical microscope (POM, Olympus, Tokyo, Japan) using magnification of 200×. The intensity of depolarized transmitted light was also registered by using a Mettler ZUFP 82 photomonitor (Mettler-Toledo International Inc., Barcelona, Spain). A small portion of PET was sandwiched between two glass cover slips and melted in a hot stage to obtain films with an average thickness of 5 μm . For optical characterization, films were heated during 3 min at the equilibrium melting temperature T_m° (280 °C) in order to erase the thermal history, as reported in the literature [5]. Then, films were crystallized under isothermal conditions for 30 min in a Mettler FP82 HT hot stage mounted in the optical microscope.

2.3. Scanning Electron Microscopy (SEM)

Micrographs of the nanoscale texture were obtained in a Topcon SM-510 scanning electron microscope (Topcon, Japan) (secondary electron beam) operating with an acceleration voltage of 15 kV, magnifications of 1000× and 20,000×, an angle of 30° and an observation distance of 7 mm. Samples were heated during 3 min at T_m° , crystallized under isothermal conditions for 30 min and finally quenched on a cold surface.

2.4. Wide Angle X-ray Diffraction (WAXD)

Wide angle X-ray diffraction (WAXD) patterns of thick samples (2 mm) were recorded in an X-ray Siemens D-5000 diffractometer (Siemens, Geratewerk Karlsruhe, Germany) with Ni-filtered CuK_α radiation generator (35 kV and 25 mA). Patterns were obtained from 5° to 60° in 2 θ at steps of 0.6° min^{-1} . Samples for WAXD analysis were heated during 3 min at T_m° , crystallized under isothermal conditions for 30 min and finally quenched on a cold surface.

2.5. Small Angle X-ray Scattering (SAXS)

Small angle X-ray scattering (SAXS) measurements were performed in the 10-meter length instrument at Oak-Ridge National Laboratory, Oak-Ridge, TN, USA. Two detector distances—namely, 1.119 and 5.119 m—were used to obtain a wide range of small angle scattering data. Absolute intensity measurements were obtained for each distance and then both curves were joined together. The collected data were radially (azimuthally) averaged in the range of the scattering vector $0.1 \leq q \leq 4.9$, where $q = (4\pi/\lambda) \cdot \sin \theta$, and $\lambda = 1.54 \text{ \AA}$. The scattering data were converted to absolute differential cross section by means of pre-calibrated secondary standards. The absolute intensity axis was in cm^{-1} . Samples for SAXS measurements were prepared as previously described for WAXD characterization.

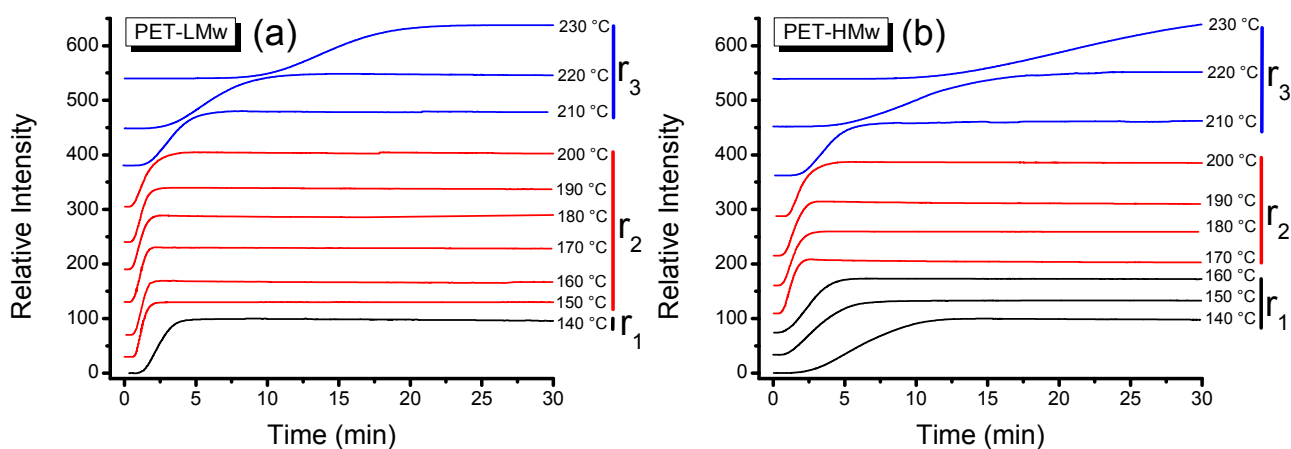
2.6. Time-Resolved SAXS/WAXD (TR-SAXS/WAXD)

Time-resolved SAXS/WAXD measurements were carried out using two linear position sensitive detectors at the X27C beam line in the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), NY, USA. The wavelength of the X-ray was 0.137 nm, the SAXS sample to detector distance was 1428 mm and the WAXD sample to detector distance was about 150 mm. Isothermal crystallization was performed using a dual-chamber temperature jump apparatus. The sample was sealed between two Kapton films (DuPont, Front Royal, VA, USA). After being equilibrated for 5 min at T_m° , the sample was rapidly jumped to a second chamber aligned in the path of the X-ray beam, where it was held at T_c for 30 min. Each time-resolved SAXS/WAXD pattern was acquired at an acquisition time of 15 s. Before each run, the air scattering was measured using an empty sample holder having two Kapton films. Each X-ray profile was corrected by subtracting the air scattering. Fluctuations of the primary X-ray beam were corrected by means of an ionization chamber. Since the sample was sealed between two Kapton windows no further corrections on the sample thickness were performed.

3. Results and Discussion

The isothermal crystallization of PET homopolymers, as a function of time, was first characterized by polarizing optical microscopy utilizing two types of analytical techniques. In the first one, polarized light in thin films (with similar thickness) was *in situ* detected with a photomonitor that registered the intensity of depolarized transmitted light (see normalized curves in Figure 1). In the second one, sequential micrographs were taken at different time intervals, where selected micrographs are presented in Figure 2.

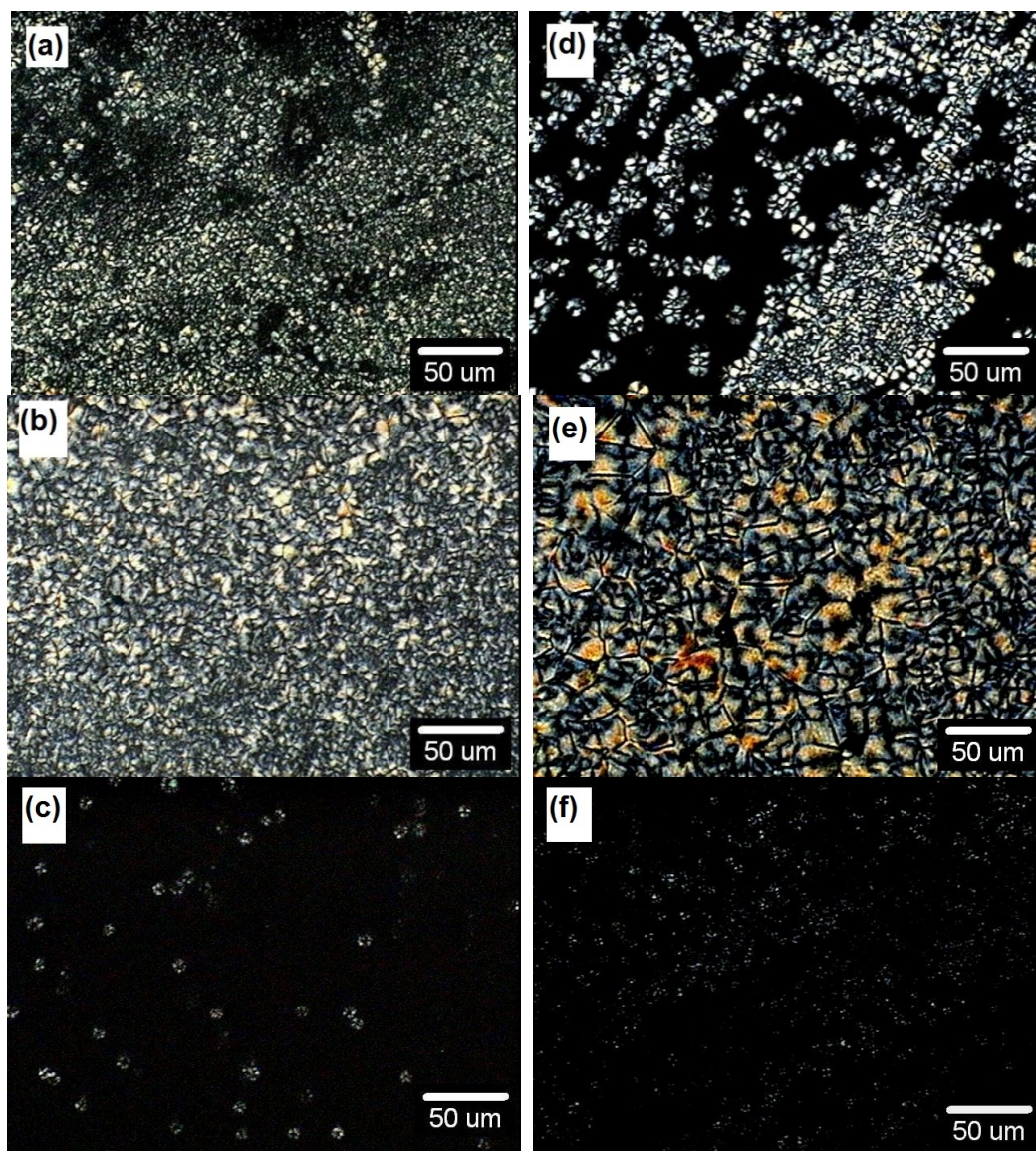
Figure 1. Evolution of transmitted depolarized light intensity during the isothermal crystallization (30 min) of PET samples at different temperatures: (a) PET-LMw; and (b) PET-HMw.



According to the shape of curves depicted in Figure 1, three different regions can be defined. In the first region (r_1), corresponding to low crystallization temperatures, the intensity increased slowly. In the second region (r_2), corresponding to intermediate T_c , a sudden increase in intensity was observed. The third region (r_3), corresponding to high T_c , exhibited a less pronounced rate of increase in intensity;

this behavior is particularly observed in high molecular weight samples crystallized at these high temperatures. At the same time, micrographs in Figure 2 showed that in r_1 and r_3 there is a partial crystallization with important amounts of amorphous material (micrographs in Figure 2a,c,d,f), where as in r_2 the material seems to be completely crystallized (micrographs in Figure 2b,e). Even though the use of a photomonitor is quite conventional for microscopic analysis, there are few reports in which this tool was used to explore the crystallization process of polymers. For instance, Bian *et al.* by using this technique found important differences in the crystallization rate of PET isothermally crystallized from low to high T_c [10]. Also, Chen *et al.* reported a similar behavior from temperatures in the regions r_2 and r_3 [11], however, these authors did not define specific morphological regions as those here described. In other studies, authors have defined differences in the crystallization of PET as a function of T_c , but only utilizing few analytical techniques, such as SEM and WAXD [6].

Figure 2. Polarizing optical microscopy (POM) micrographs of isothermally crystallized (5 min) of PET samples at different temperatures. PET-LMw: (a) 140 °C; (b) 180 °C; and (c) 230 °C. PET-HMw: (d) 140 °C; (e) 180 °C; and (f) 230 °C.



Figures 1 and 2 also show differences in crystallization as a function of molecular weight. In general, the increase of this variable produces both a systematic decrease in the crystallization rate and an increase in the amount of amorphous material. This behavior is attributed to the fact that a bigger macromolecular chain will require a greater amount of energy to effectively diffuse on the crystal growth interface; thus, the material crystallizes at a slower rate and facilitates the generation of larger sets of amorphous sections.

Representative micrographs of each crystallization region for PET, as a function of T_c , are presented in Figure 3. The typical spherulite morphology is observed in regions r_1 (Figure 3a) and r_2 (Figure 3b). In r_3 (Figure 3c), the optical texture is a little different and seems to correspond to a disk-like morphology. However, by SEM analysis (Figure 4a–c are regions r_1 , r_2 and r_3 , respectively) such disk-like morphology was not detected. Also, the radius of spherulites in r_3 was much bigger compared to those observed in the other two regions. Similar results for PET were found by van Antwerpen and van Krevelen, which have determined a maximum spherulite radius for the highest T_c (200–210 °C) [4].

Figure 3. POM micrographs of isothermally crystallized PET-HMw at (a) 200 °C and 1 min; (b) 220 °C and 5 min; and (c) 230 °C and 12 min.

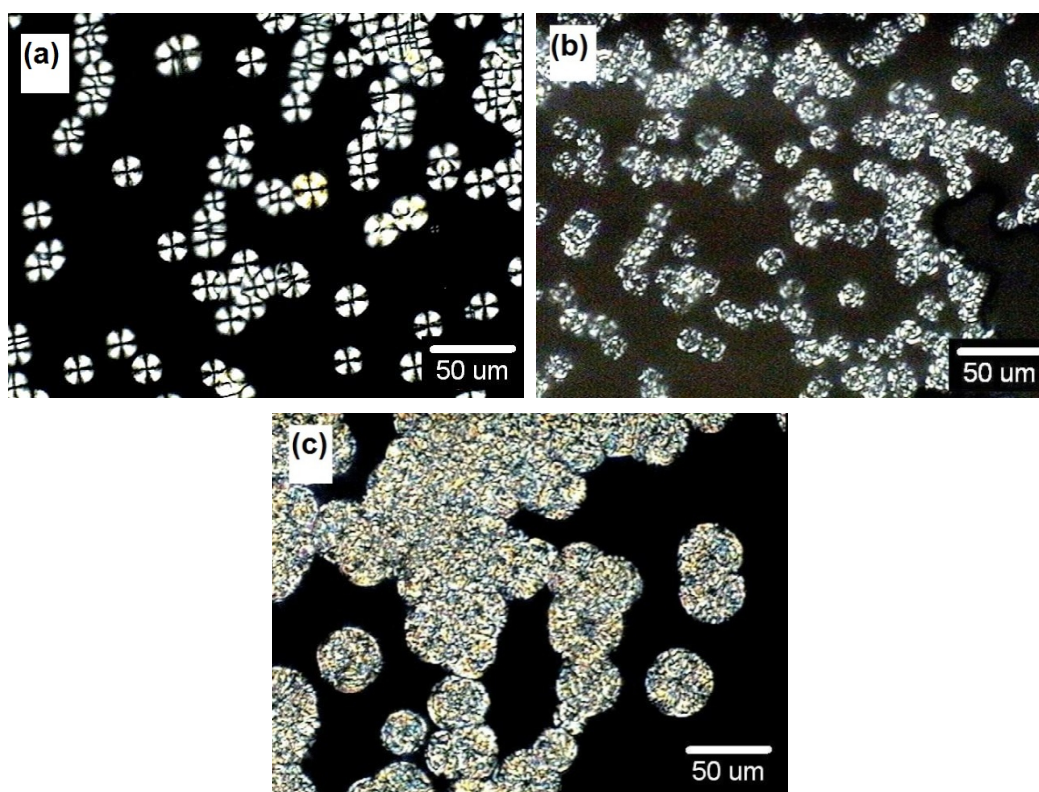
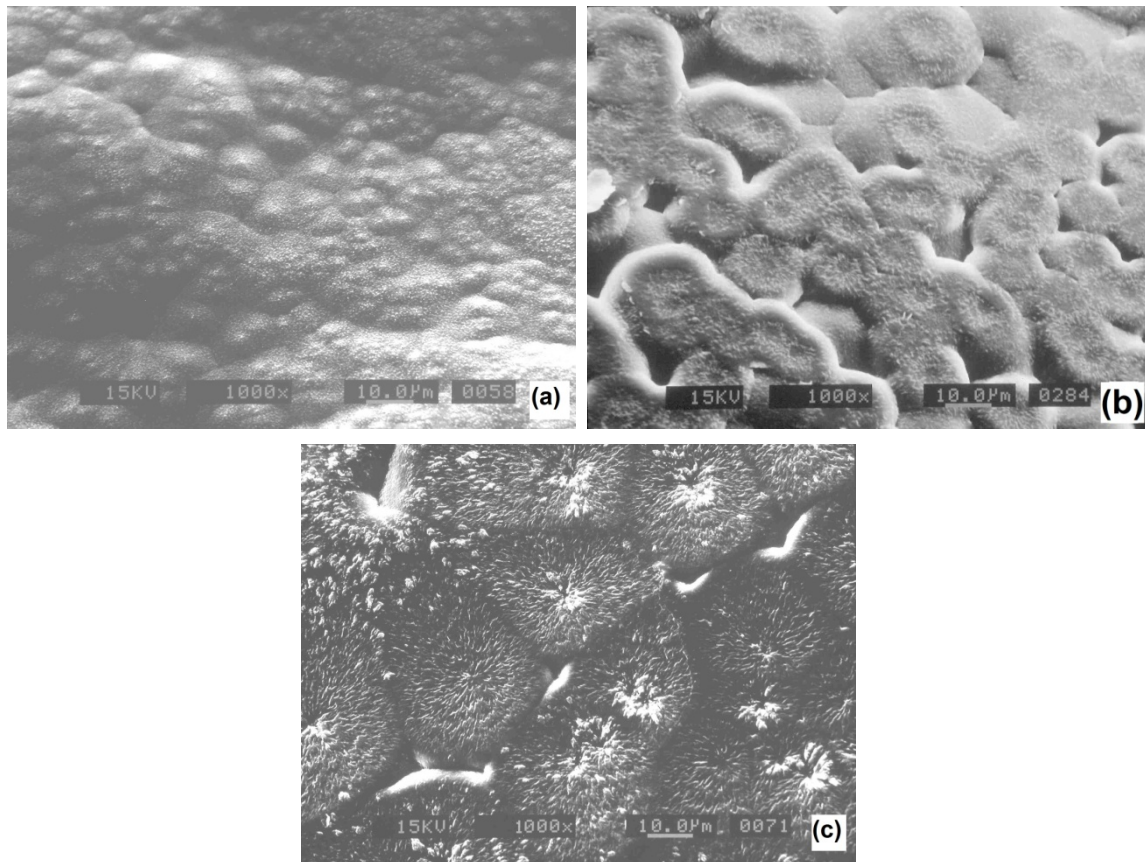


Figure 4. SEM micrographs of isothermally crystallized (30 min) PET-HMw at different temperatures: (a) 140 °C; (b) 200 °C; and (c) 220 °C.



On the other hand, Hoffman *et al.* reported three different growth regimes [9]. In one of them, the nucleation rate is high while the diffusion rate is low; in the opposite regime, contrarily, the nucleation rate is low while diffusion rate is high. Then, it is expected that at one temperature limit, the formation of the nuclei dominates (high nucleation), while at the other one, diffusion of the material dominates and produces a small amount of nuclei (low nucleation). As seen in the POM and SEM micrographs in this study, high nucleation dominates at lower T_c , while diffusion dominates at higher T_c .

The Avrami equation was applied to data obtained from isothermal crystallization experiments (Figure 1) and results are shown in Figure 5 [12–14]. For the range of temperatures in r_2 , a deviation of the initial slope could be associated to secondary crystallization (Table 1), and this event is occurring in conjunction or in a subsequent stage with respect to the primary crystallization mechanism [15]. In general, secondary crystallization is insignificant at low T_c (140–170 °C) and high T_c (220–230 °C), whereas at intermediate T_c (180–210 °C) it becomes important. For PET-LMw, the Avrami exponent (n) is close to 3.0 in r_1 and r_2 , but it attains values near 4.0 in r_3 . For a spherulite morphology, values around 3 indicate an instantaneous nucleation along with a shape of growth, which produces small amounts of amorphous material [15]. Values near 4 indicate the same shape growth, although in this case the crystallization is homogeneous and leads to the formation of spherulites of different size. Micrographs in Figure 3 corroborate these predictions. The two slopes in r_2 suggest the formation of two crystal families. For PET-HMw, the exponents were on average close to 2.5 and 3 for r_1 and r_2 , respectively. They were even close to 4 in r_3 . For a spherulitic morphology, the value 2.5 indicates

homogeneous nucleation with a shape growth by diffusion, producing important amorphous zones as can be seen in Figure 3. These exponents agree with those reported for some authors. For instance, Rybníkar reported an $n = 4$ for $T_c > 217$ °C [16], while Keller *et al.* found n values close to 3 in the range of 170–220 °C, which is consistent with results obtained at intermediate and high T_c in the present work [17].

Figure 5. Avrami plots obtained from transmitted depolarized light intensity of different PET samples isothermally crystallized at different temperatures: (a) PET-LMw; and (b) PET-HMw.

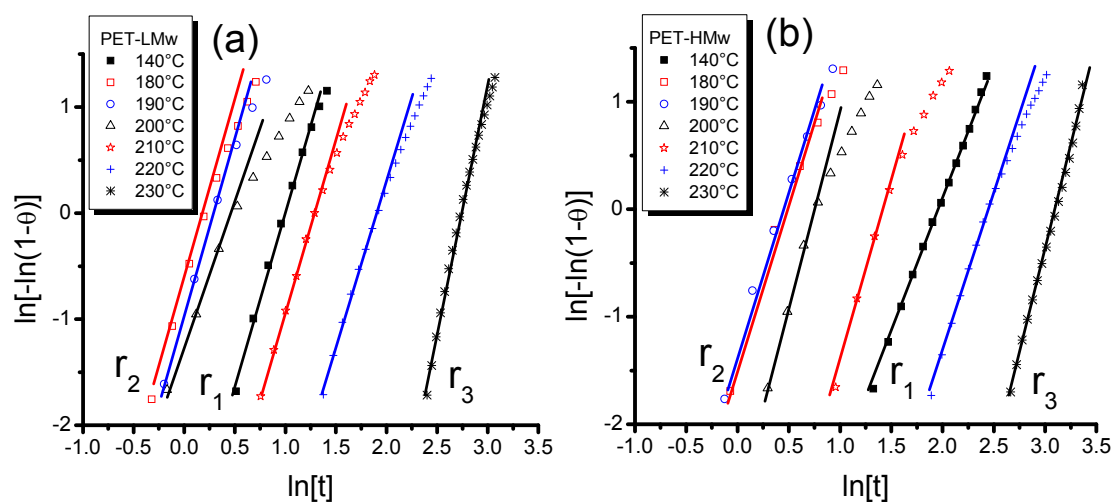
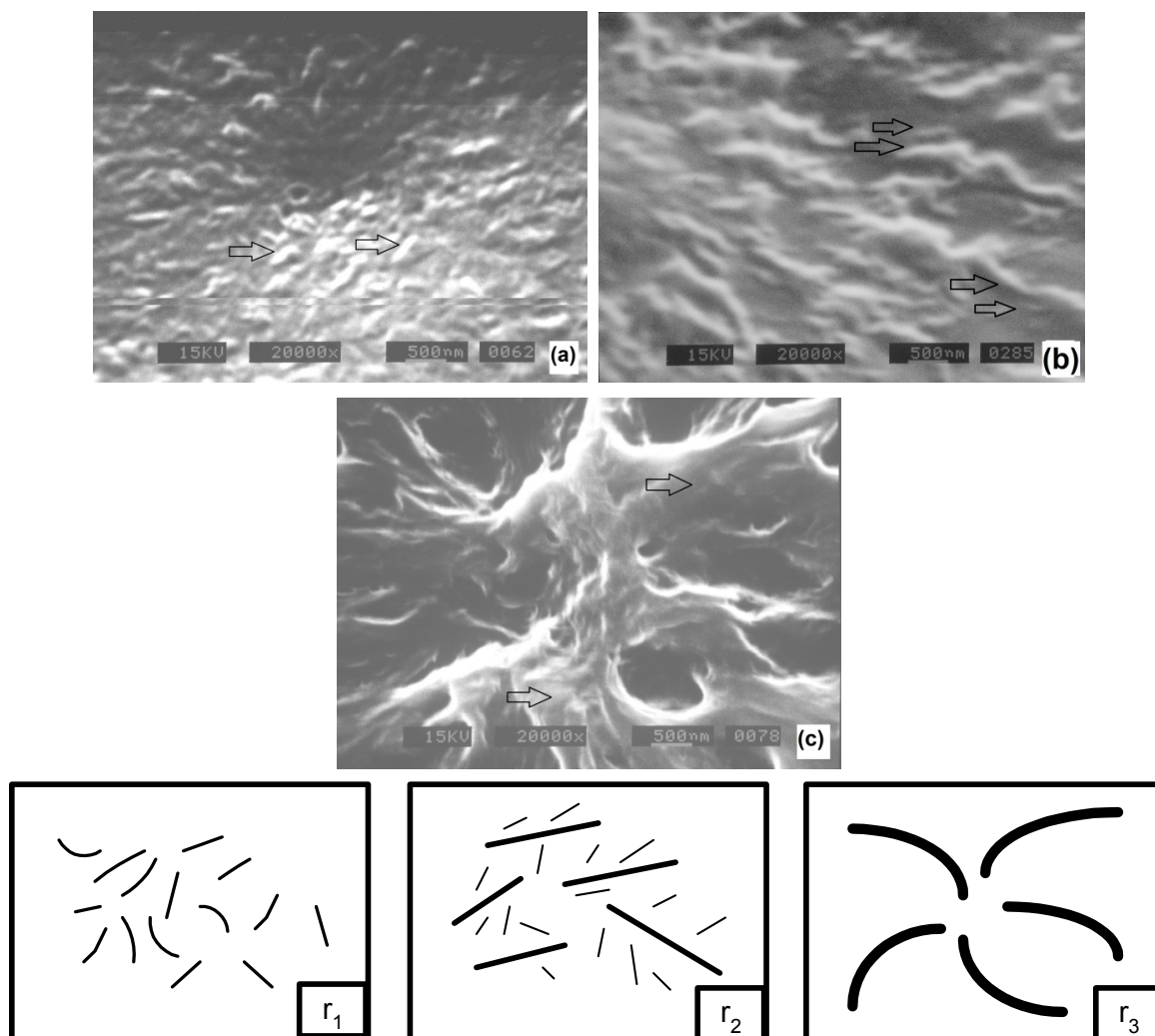


Table 1. Morphological parameters from Avrami analysis of isothermally crystallized PET samples at different temperatures.

Temperature	n LMw	n HMw	Secondary crystallization	Slopes	Crystalline families
140 °C	2.8	2.2	Null	1	1
150 °C	3.1	1.9	Low	1	1
160 °C	2.9	2.5	Low	1	1
170 °C	3.3	3.0	Low	1	1
180 °C	3.3	3.3	Medium	2	2
190 °C	3.0	3.1	Medium	2	2
200 °C	2.7	3.6	High	2	2
210 °C	2.9	3.3	Medium	2	2
220 °C	3.7	3.1	Low	1	1
230 °C	4.7	3.9	Null	1	1

The presence of one or two crystalline lamellar stack families was also corroborated by SEM, as it is observed in micrographs depicted in Figure 6. At 160 °C (Figure 6a or r_1) and 220 °C (Figure 6c or r_3) crystals are uniform, although in r_1 they are small and thin while in r_3 they are big and thick (arrows in the figure). In contrast, at 200 °C (Figure 6b or r_2) a mixture of crystals, or two crystalline lamellar stack families of different size, is readily apparent (arrows in the figure). The observed thicker crystals in r_3 is in agreement with crystallization studies on PET and some other polymers like low density polyethylene (LDPE), but the presence of the two crystal lamellar stack families was not reported [6,18].

Figure 6. SEM micrographs of isothermally crystallized (30 min) PET-HMw at different temperatures: (a) 140 °C; (b) 200 °C; and (c) 220 °C.



Wide angle X-ray diffraction patterns of PET-LMw samples crystallized at different T_c are shown in Figure 7a. Their analysis indicates a triclinic structure for this polymer, as it was reported by Farikov *et al.* [19]. From patterns, a plot of crystalline degree *versus* T_c (Figure 7b) was obtained and again three regions can be clearly delimited.

In r_1 , the crystalline degree (% X_c) for PET-HMw is low (near 30%) and remains almost constant along this region (140–160 °C), while for PET-LMw this parameter is higher (~35%) but limited to only one T_c (140 °C). The constant % X_c values observed for high molecular weight PET in r_1 suggest that mobility or diffusion of chains remains similar in this temperature region. From r_1 to r_2 , there is a sudden increase in crystallinity, and in r_2 the crystallinity increases gradually up to a maximum (210 °C). This behavior can be associated with an increase in molecular diffusion that favors the molecular arrangement. In r_3 the crystalline degree shows a sharp decrease that can be explained in terms of a combination of molecular diffusion and molecular vibration. Both increase with temperature, although the former favors the crystal formation and the later perturbs it and becomes dominant at the highest temperatures. In crystallizing PET for longer times at different T_c , Groenickx *et al.* found that crystallinity increases monotonically up to a maximum [6]. For the highest T_c , no decrease in crystallinity

was observed due to the relatively long time (17 h) used in their experiments [6]. For instance, Karagiannidis *et al.* reported crystalline degree of 31.4% for a PET sample crystallized at 115 °C for 30 min [20], and Zhang *et al.* reported a 28.6% and 30.9% values for samples crystallized at 110 °C for 20 and 40 min respectively, which is consistent with results obtained at low T_c in the present work [21].

Figure 7. (a) Wide angle X-ray diffraction (WAXD) patterns of isothermally crystallized (30 min) PET-LMw at different temperatures; and (b) Crystalline degree of isothermally crystallized PET samples at different temperatures. Data were obtained from WAXD patterns.

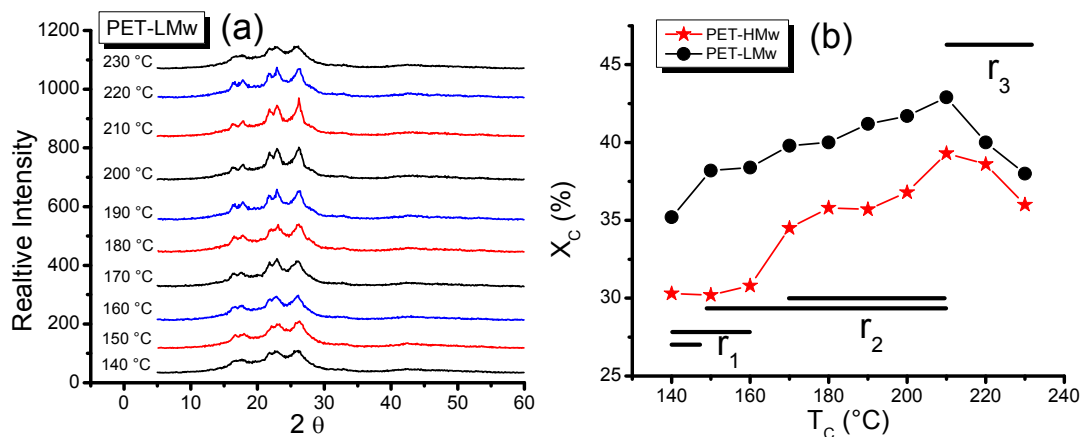


Figure 8a shows the evolution of the X-ray diffraction patterns, as a function of time, obtained by using time-resolved synchrotron radiation (TR-WAXD) and the crystalline degree (% X_c) was plotted against time in Figure 8b,c. Samples isothermally crystallized for 30 min were chosen for this analysis. It can be seen that at intermediate T_c (200 °C) samples crystallized very fast, while at high T_c (220 °C) crystallization proceeds very slowly. At low T_c (160 °C) the crystallization rate is moderately lower than that observed at intermediate T_c , although this variable depends on molecular weight as it was demonstrated by POM analysis (Figure 1), where differences in crystallization curves were observed as the molecular weight increased.

Figure 8. (a) Time-resolved WAXD patterns registered during the isothermal crystallization (30 min, 160 °C) of PET-LMw; Crystalline degree of isothermally crystallized PET at different temperatures: (b) PET-LMw; and (c) PET-HMw. Data were obtained from time resolved WAXD patterns.

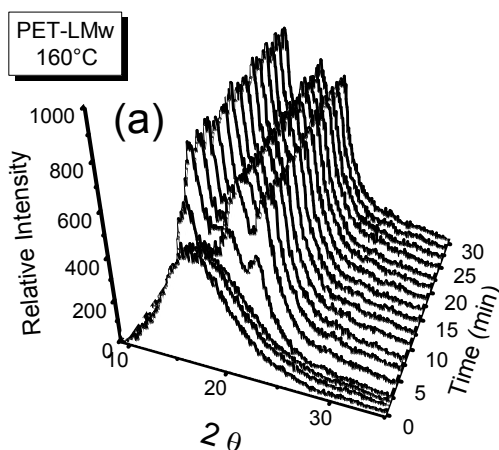
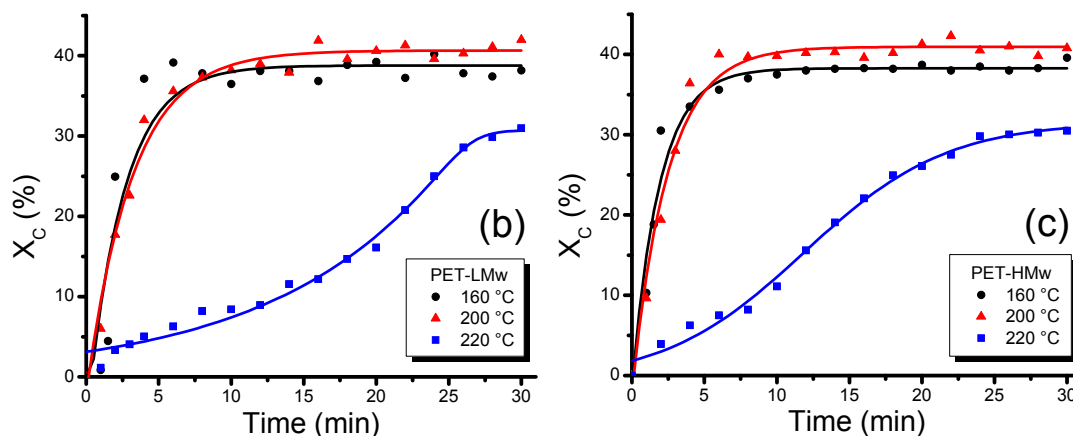


Figure 8. Cont.



Morphological parameters of semi-crystalline polymers like the average long period (L), average crystalline lamellar thickness (l_c), average interlamellar amorphous layer thickness (l_a), electron density difference between two phases ($\Delta\rho$), invariant (Q), among others, can be determined by means of small angle X-ray scattering (SAXS) and time-resolved SAXS. These parameters are calculated by transforming the reciprocal space intensity data into a real-space by using mathematical models like the normalized correlation function $\gamma_1(r)$ or the interface distribution function $g_1(r)$ [18,22]. In the present work, the self correlation triangle method was used to solve $\gamma_1(r)$; calculations and simulations were done by using mathematical software (Matcad 4 and Origin 7) [23,24].

Figure 9 shows the scattering vector (q) versus the scattering intensity $I(q)$ profiles for PET samples isothermally crystallized for 30 min. It can be seen that the maximum of curves decreases monotonically with temperature, which is indicative of an increment of the long period [25]. The l_c , l_a and L parameters are obtained by simulation of $\gamma_1(r)$ (Figure 10a,b), however, it is not clear which calculated value corresponds to l_c (or l_a) [22]. In this respect, some authors have proposed that the big one corresponds to l_c [24–29], while some others have proposed the opposite [6,22,30,31]. In the present work, the small calculated value was assigned to l_c because when it was used to calculate the crystalline degree (Figure 10c), results agreed well with data obtained by WAXD [22].

Figure 9. SAXS patterns of isothermally crystallized (30 min) PET at different temperatures: (a) PET-LMw; (b) PET-HMw.

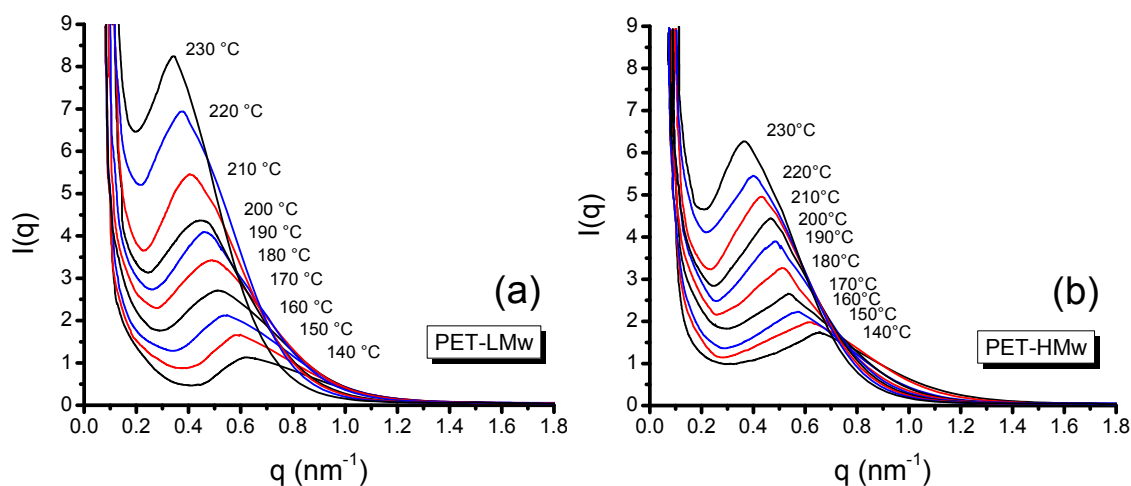


Figure 10. Morphological parameters (L , l_a and l_c) of isothermally crystallized PET at different temperatures: (a) PET-LMw; (b) PET-HMw; and (c) Crystalline degree of isothermally crystallized PET. Data were obtained from SAXS patterns.

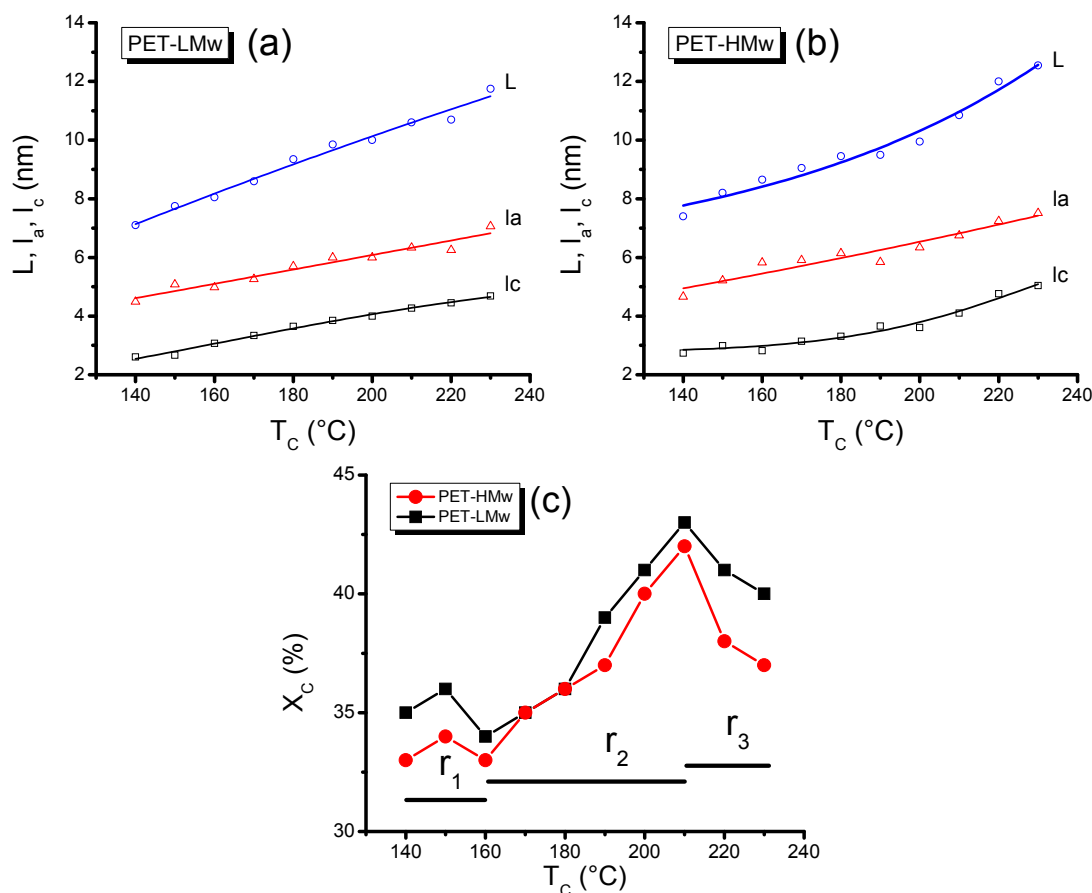


Figure 10 shows that L , l_a and l_c increase with T_c , as deduced from SEM and POM micrographs, where thicker crystals were registered, respectively. As expected, the increase in molecular weight has produced higher values of l_a . Again, this observation relates well with the increment of amorphous regions observed previously by WAXD results. The increase of l_c as a function of T_c for PET and other polymers, like LDPE, has been reported and analyzed by other authors [6,18].

Differences in electron density ($\Delta\rho$) provide information about the crystal perfection. Figure 11a shows a sharp increase of this variable at low T_c (140–180 °C) and relatively constant values at high T_c (190–220 °C). This observation indicates that the crystal perfection is substantially improved in the low temperature region and that it remains practically unaffected at higher temperatures.

The power of dispersion in characterized samples, as a function of T_c , is indicated by the invariant Q patterns shown in Figure 11b. It can be noticed that Q increases sharply up to a maximum (intermediate T_c), then it decreases slowly. These curves are comparable to those obtained by WAXD (Figure 7) that also showed a maximum of crystalline material at intermediate T_c .

Figure 11. (a) Differences in electron density ($\Delta\rho$); and (b) Invariant (Q) of isothermally crystallized PET at different temperatures.

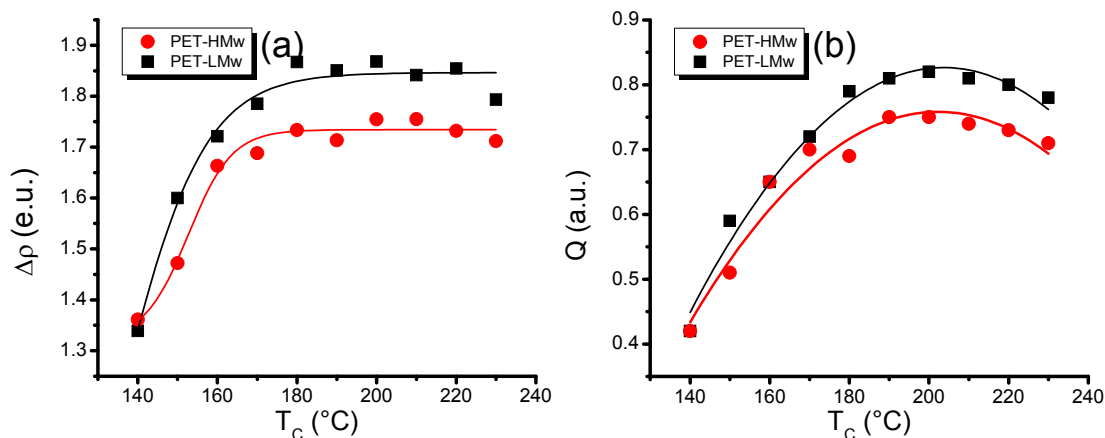


Figure 12a shows the time resolved SAXS patterns for PET-LMw. By applying the $\gamma(r)$ function to curves, the morphological parameters L , l_c , l_a were calculated and plotted in Figure 12b,c [18]. A retarding effect can be seen at the highest T_c (220 °C), which is attributed to the slow crystallization process occurring at this temperature. Similar to SAXS, a general increase is observed in the value of morphological parameters as a function of T_c . It can be noticed that l_c increases with time only at high T_c (220 °C), while it remains almost unchanged at the other considered crystallization temperatures (160 and 200 °C). This behavior indicates that there is a lamellar thickening during crystallization. Simultaneously, the decreasing value of l_a at high T_c (220 °C) indicates that part of the amorphous material is incorporated into crystal structures.

Time-resolved measurements for the electron density ($\Delta\rho$) in crystallized samples are shown in Figure 13. It can be noticed that the highest values of $\Delta\rho$ are presented at high T_c , indicating a higher crystalline perfection. The increase in molecular weight reduces the value of $\Delta\rho$ for samples crystallized at identical T_c , indicating a minor crystalline perfection for the highest molecular weight sample (PET-HMw).

Figure 12. (a) Time-resolved SAXS patterns of isothermally crystallized (30 min) PET-LMw at different temperatures; Evolution of morphological parameters (L , l_a and l_c) (b) PET-LMw; and (c) PET-HMw. Data were obtained from time resolved SAXS patterns.

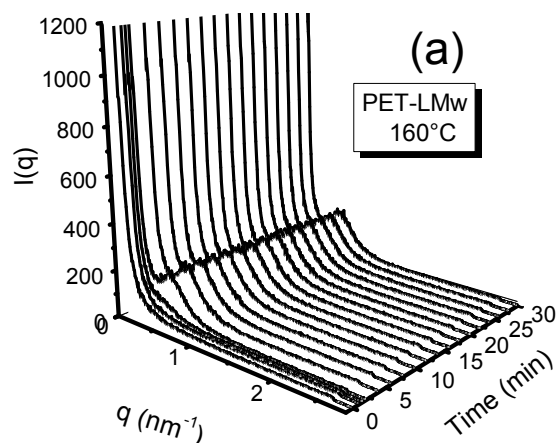


Figure 12. Cont.

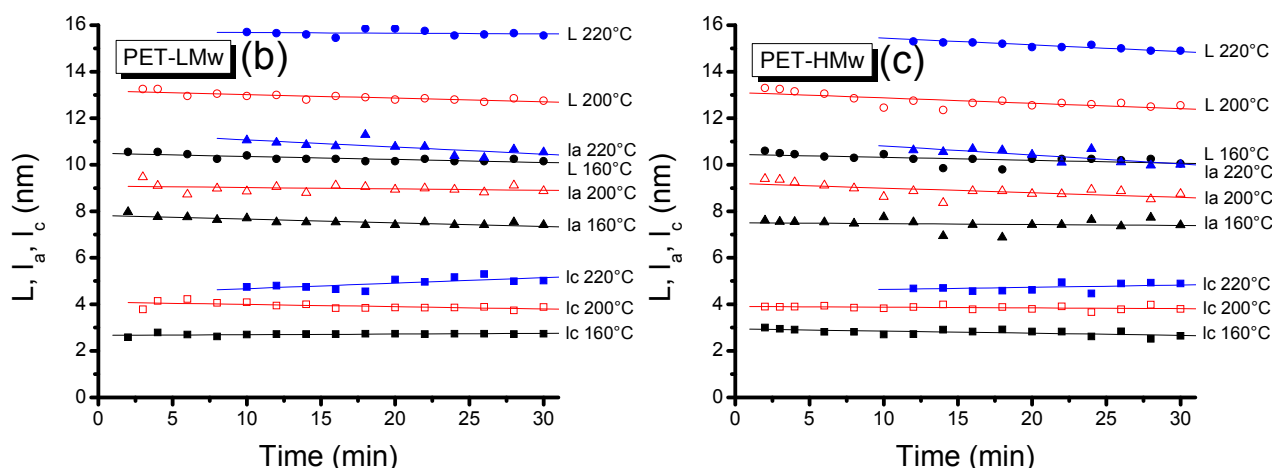
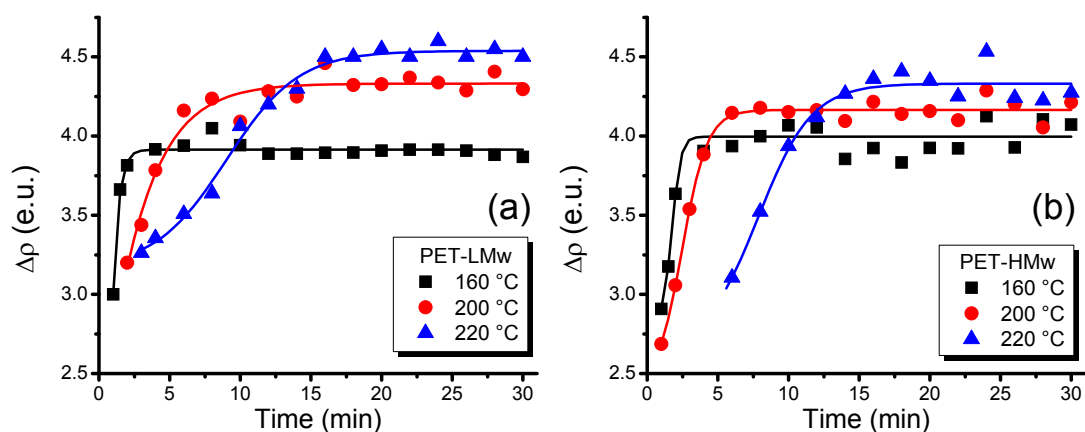


Figure 13. Evolution of electron density ($\Delta\rho$) of isothermally crystallized PET at different temperatures: (a) PET-LMw; and (b) PET-HMw. Data were obtained from time-resolved SAXS patterns.

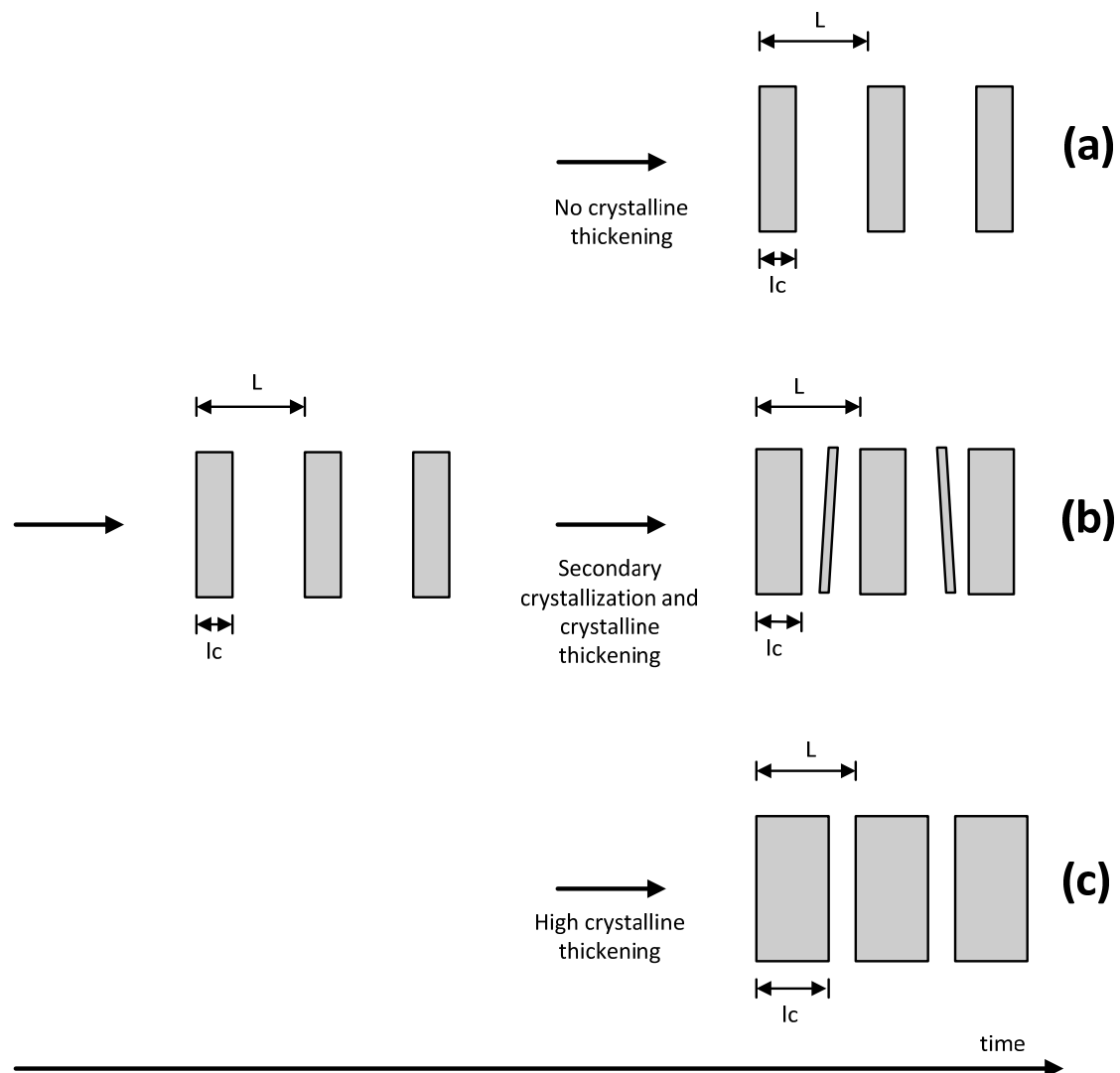


In addition, it is expected the formation of imperfect and thin crystals in the high nucleation regimen (low T_c) due to the low diffusion of the material, while bigger and more perfect crystals are expected in the regime where diffusion predominates (high T_c). In the present study, SEM, SAXS and TR-SAXS were used to analyze this behavior in a wide temperature range. The results obtained are in accordance with the growth regimes reported by Hoffman *et al.* [9].

In order to provide a concise idea of the isothermal crystallization process for PET, in a wide temperature range, it is necessary to consider the three aforementioned regions r_1 , r_2 and r_3 , each one following a different morphological pathway. In this respect, a model is proposed for each region.

In r_1 (low T_c) the morphology was characterized by thin crystalline structures (SEM) and important amorphous zones (POM) or low crystalline degrees (WAXD). On the other hand, the Avrami analysis showed the presence of only one crystalline family, with relatively small values of l_c , L and $\Delta\rho$ (SAXS) with respect those found in the other regions. As a function of time, the l_c (TR-SAXS) remained constant indicating that there is no crystal thickening during the process. From these results, a morphological model is proposed in which the initially formed thin crystalline structures do not evolve as a function of time as it is shown in Figure 14a.

Figure 14. Morphological model for the isothermal crystallization of PET: (a) Low temperatures (region 1); (b) Intermediate temperatures (region 2); and (c) High temperatures (region 3).



In r_2 (intermediate T_c), both thin and thick structures were observed (SEM). Here, the highest crystalline degree was obtained (POM and WAXD) and associated with a high content of secondary crystals as detected by the Avrami analysis. The crystal perfection (SAXS) was higher than that observed in r_1 , evolving gradually with time (TR-SAXS). From these results, the proposed model consists of thick primary structures that coexist with thin and small secondary structures. For this region, it is possible that the primary crystals are first formed, then, the formation of secondary crystals and thickening of primary crystals occurs simultaneously, as it is schematized in Figure 14b.

In r_3 (high T_c), thick structures (SEM) with significant amorphous regions were observed (POM and WAXD). Only one crystalline family was appreciated by the Avrami analysis. The l_c , L and $\Delta\rho$ were higher with respect to those measured for the other two regions (SAXS). The l_c also increases as a function of time (TR-SAXS) in this region. Here, the proposed model considers a significant crystal thickening that occurs during crystallization, as it is shown in Figure 14c.

4. Conclusions

The isothermal crystallization of PET with different molecular weight was studied in a wide temperature range by using different techniques (POM, SEM, WAXD, SAXS, TR-WAXD and TR-SAXS). Results revealed the existence of three different regions as a function of crystallization temperature. The first region (low T_c) was characterized by a low crystallization process leading to thin crystalline structures and important amorphous zones. Here, only one crystalline family was encountered with smaller values of l_c , L and $\Delta\rho$ in respect to the other two regions. In this region, l_c remained constant as a function of time indicating that there is no crystal thickening during the process. The increase in molecular weight has produced low crystalline degrees and relatively small l_c , both associated with diffusion problems of long molecules. The second region (intermediate T_c) evidences a faster crystallization rate. Here, the highest crystallinity was obtained and the morphology was composed of thick primary structures coexisting with thin and small secondary structures. The crystal perfection was higher than that determined in the previous region. A similar effect in the crystalline characteristics was observed when the molecular weight was increased. The third region (high T_c) showed a marked decrease in the crystallization rate leading to significant amorphous regions and the formation of only one crystalline family characterized by thick lamellar structures. The lamellar thickness, as well as the crystal perfection, was higher with respect to the other two regions. It is important to mention that in this region l_c increases as a function of time indicating an important thickening of crystals. Again, an increase in molecular weight has produced a decrease in crystallization and crystal perfection. Finally, all these results were concisely explained through morphological models.

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Conflicts of Interest

The authors declare no conflict of interest.

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