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Structural Reorganization in Poly(butylene terephthalate) during Fusion

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ABSTRACT: A detailed investigation of the reorganization processes occurring in the crystalline phase of poly(butylene terephthalate) (PBT) during fusion was performed by temperature-modulated differential scanning calorimetry (TMDSC). Quasi-isothermal TMDSC analyses were conducted for extended times at different temperatures in the whole melting range, revealing different degrees of reversible melting. The latent heat involved in the fusion/recrystallization/crystal-perfection processes was found to decrease with time for the quasi-isothermal analyses performed at temperatures below 500 K. At higher temperatures, on the contrary, recrystallization prevailed with a continuous increase of the apparent reversing heat capacity as a function of time. The multiple melting behavior of PBT, often reported in the literature, was correlated with the results of the present quasi-isothermal TMDSC investigation.

Introduction

Fusion of polymers is a complex phase transition, as it may involve, besides the plain melting process, various transformations of the metastable crystal structure, including partial recrystallization, annealing, and perfection of the initial crystals.[1] One of the main experimental techniques that has been used during the years to study the fusion process in polymers is differential scanning calorimetry (DSC).[1,2] With the support of other techniques, as for example optical microscopy or X-ray diffraction, a DSC curve can allow to identify the main parameters that characterize polymer melting as well as to recognize the occurrence of reorganization processes of the crystal phase, generally connected to the presence of multiple endotherms or exotherms, or to allow identification of the existence of different crystal morphologies from the position and breadth of the melting peaks.

In recent years, a new modification of DSC, temperature-modulated DSC, usually abbreviated as TMDSC, has also been used to investigate fusion in polymers.[3,4] With TMDSC it is possible to superimpose a periodic temperature variation on the conventional linear scan. In this way, by means of a series of calculation procedures easily available in the literature,[5−7] the experimentally measured heat flow rate signal (Φ) can be separated into a total contribution (approximately equal to a conventional DSC measurement with the same underlying heating rate) by sliding averages over the modulation period and a periodic part, obtained from the amplitude of signal due to modulation only. The modulus of the complex heat capacity, calculated from the periodic component of the heat flow rate, is often called reversing heat capacity, even if reversing and nonreversing processes both contribute to it.[8−10] Unfortunately, separation of reversing and nonreversing contributions is often not quantitative when processes with high latent heats (typical of first-order transitions) are analyzed in TMDSC with an underlying heating rate.[8−10]

Despite these limitations, TMDSC can provide useful information on both kinetic and equilibrium aspects of the melting/crystallization process in polymers. Quantitative data on reversible melting at a given frequency modulation can be obtained only in absence of irreversible processes, i.e., by performing long-time quasi-isothermal analyses with small oscillations around a base temperature (T_0). These small temperature variations, typical of TMDSC, allow to monitor the time evolution of specific heat capacity (c_p) at T_0, a measurement that is impossible to perform with simple isothermal DSC.[11] Any slow change of the crystallization, melting, or crystal-perfection extent results in a corresponding variation in the reversing c_p signal. If a constant reversing c_p value is ultimately reached when all irreversible phenomena have faded away, the measured reversing specific heat capacity can be compared to the equilibrium values extrapolated from measurements outside the transition region. Any deviation of the reversing c_p extrapolated to infinite time from the equilibrium c_p value indicates the occurrence of thermal events in a process that is completely reversible with respect to the temperature modulation. Such deviations are generally observed for semicrystalline polymers analyzed in the melting range and are attributed to local equilibria at the interface between crystal and melt, probably involving the fold surfaces of the polymeric nanocrystals, their side surfaces, or both.[4,12−15]

An alternative route to quasi-isothermal analysis consists of a detailed analysis of the modulated heat flow rate profile within each modulation period when measurements are conducted with a nonzero underlying heating rate.[9,16] This procedure, adopted for a preliminary investigation of the melting process of poly(butylene terephthalate) (PBT),[16,17] allowed to demonstrate that fusion in PBT does not proceed through a three-step process consisting of fusion of a certain amount of original crystals, followed by recrystallization/

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annealing/crystal-perfection and final melting of the more perfect crystals, partly formed during primary crystallization and partly through the recrystallization process, as revealed by conventional DSC analysis, but that, during a heating scan, the just melted defective PBT crystal fractions immediately recrystallize into more stable structures while fusion occurs in other portions of the semicrystalline sample. These continuous fusion/recrystallization/annealing/crystal-perfection processes are not induced by the modulation of temperature but take place also inside a single semiperiod of the temperature modulation.[16]

Unfortunately, the type of analysis based on examination of the modulated heat flow rate profile is only qualitative. At present, quantitative data on the melting process of polymers can be obtained only with quasi-isothermal TMDSC analyses, whose results on the PBT melting are illustrated in this contribution. Quantitative data on fusion are needed to gain insight into the complex nanophase structure of semicrystalline polymers to fully understand the processes related to the formation and evolution of the various nanophases that have been, at present, clarified only in part. The results of these investigations are ultimately expected to provide a direct link between the thermal properties and the molecular structure of polymers.[4]

Experimental Section

Poly(buthylene terephthalate) (PBT) of molar mass M_n = 44 000 g/mol and M_w = 81 000 g/mol was purchased from Sigma-Aldrich Corp. The sample chips were compression-molded with a Carver Laboratory Press at a temperature of 523 K for 3 min, without any applied pressure, to allow complete melting. After this period, a load of about 0.5 ton was applied for 2 min. Successively the sample was quickly cooled to room temperature by means of cold water circulating in the plates of the press.

DSC and TMDSC measurements were performed with a Perkin-Elmer dynamic differential scanning calorimeter DSC 7 (DDSC). The instrument was calibrated in temperature with high-purity standards (indium, naphthalene, and zinc) at 3 K/min, according to the procedure for standard DSC. The heat flow rate was initially calibrated with the heat of fusion of indium and then refined with a run of two empty aluminum pans and a calibration run with sapphire as a standard.[18]

Dry nitrogen was used as purge gas at a rate of 35 mL/min. To reduce temperature gradients, the sample mass was kept small, approximately equal to 4 mg. A fresh sample was employed for each analysis in order to minimize thermal degradation.

The thermal history of PBT before the quasi-isothermal TMDSC analyses was identical to that reported in ref 16. The following test procedure was used: each compression-molded PBT sample was heated from room temperature to 523 K, maintained at this temperature for 3 min, and then quickly cooled to 473 K. At this temperature, PBT crystallization is fast, and the leveling off of the DSC trace occurs within 5 min. Nevertheless, the sample was kept at 473 K for 30 min to improve crystal perfection. PBT was then heated from 473 K to the chosen base temperature for quasi-isothermal modulation (T_0) using the dynamic temperature program that is obtained through a sawtooth modulation in the Perkin-Elmer DDSC. The underlying heating rate (q) was 0.5 K/min, the temperature amplitude (A_T) 0.2 K, and the modulation period (p) 120 s. When the temperature reached T_0, quasi-isothermal analyses were started with A_T = 0.2 K and p = 120 s. Each quasi-isothermal measurement was extended for 6 h (in some cases, indicated below in the text, for 7 h). At the end of the quasi-isothermal analysis, the sample was heated from T_0 to 512 K at a scanning rate of 3 K/min.

The reversing specific heat capacity (c_p) was calculated from the ratio of the amplitudes of heat flow rate and temperature, after approximation of the experimental modulated data to a Fourier series:[19]

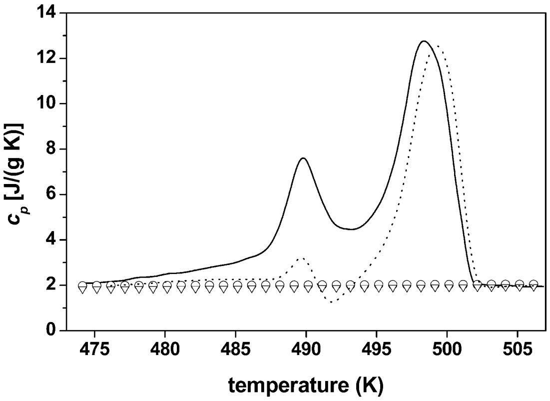

Figure 1. Apparent total specific heat capacity ($c_{p,\text{total}}$, dashed line) and apparent reversing specific heat capacity (c_p, solid line) of PBT isothermally crystallized at 473 K for 30 min as a function of temperature during heating (p = 120 s, A_T = 0.2 K, q = 0.5 K/min). The specific heat capacity of the solid and liquid PBT (∇ and ○, respectively) are from the ATHAS data bank.[22]

$$c_p(\omega,\nu,t) = \frac{\langle A_{\Phi,\nu}(t)\rangle}{\langle A_{T,\nu}(t)\rangle}\frac{K(\nu,\omega)}{m\nu\omega} \tag{1}$$

where ν is the order of the harmonic, ω is the base frequency, m is the mass of the sample, and $K(\nu,\omega)$ is the frequency-dependent calibration constant. The modulation period used (p = 120 s) was sufficiently high to provide a calibration constant for the apparent reversing heat capacity equal to 1. The reversing c_p values reported in this contribution were obtained from the first harmonic of the Fourier series. Since the sawtooth temperature profile consists only of odd harmonics, the fact that the even harmonics of the heat flow rate response were found zero during the quasi-isothermal treatments was an indication that linear and stationary conditions are perfectly satisfied with the operative conditions used in this study.[20]

Results and Discussion

Time Evolution of the Structural Reorganizations of the Crystal Phase at Selected Temperatures. The DSC and TMDSC curves on fusion of PBT usually display two major peaks.[16,17,21] A detailed analysis of the melting process of PBT by conventional DSC and TMDSC with a nonzero underlying heating rate has been presented in ref 16. The apparent total and reversing specific heat capacities (c_p) of PBT, as reported in ref 16, are illustrated in Figure 1 as they serve as a basis for the present discussion. The small difference in peak position in Figure 1 arises from the approximations that the mathematical treatment of the modulated data (eq 1) introduces, due to the high amount of latent heat evolved and absorbed by the sample during the phase transition.[8-10]

To complete the investigation on melting behavior of PBT, presented in refs 16 and 17, detailed quasi-isothermal analyses were performed. Initial measurements were conducted by modulating at 489.6 and 498.4 K, the temperatures corresponding to the two maxima of the reversing specific heat capacity peaks from the TMDSC scan shown in Figure 1.

The time evolution of the apparent reversing specific heat capacity at 489.6 and 498.4 K, calculated with eq 1, is displayed in Figure 2. The amplitude of temperature oscillations remains constant for the whole time

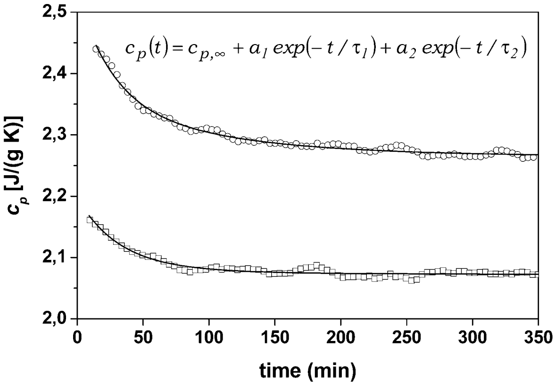

Figure 2. Time dependence of the apparent reversing heat capacity of PBT during quasi-isothermal measurements at $T_0 = 489.6$ K (□) and $T_0 = 498.4$ K (○); $p = 120$ s, $A_T = 0.2$ K.

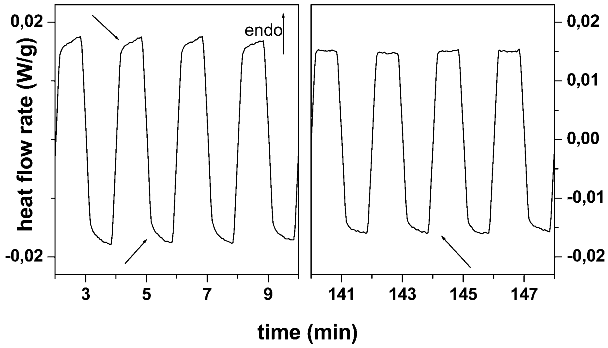

Figure 3. Modulated heat flow rate profile for PBT at different times of the quasi-isothermal measurement at $T_0 =$ 498.4 K. The arrows highlight endothermic and exothermic events.

of analysis, as expected for a power compensation calorimeter. The heat flow rate amplitude, instead, gradually decreases with time, as a consequence of the decreasing amount of latent heat that is evolved and/or absorbed by the sample during the quasi-isothermal measurement. This results in a decrease of the apparent reversing c_p with time, as usually observed for semicrystalline polymers of sufficiently high molar mass.[4] The trend is typically a double-exponential decay, with the relative equation shown in the upper right corner of Figure 2. The two relaxation times τ_1 and τ_2, that are commonly attributed to irreversible processes occurring at the interface between the metastable crystals and the surrounding melt during the analysis,[4] are found to be of the order of 10−12 and 60−100 min, respectively, for the two analyzed temperatures.

The kinetics of recrystallization and crystal perfection was followed by a close inspection of the modulated heat flow rate profiles, as presented in Figure 3a,b for the quasi-isothermal analysis conducted at $T_0 = 498.4$ K. At the initial stages of the quasi-isothermal treatment, both endothermic and exothermic events take place within the same modulation period (Figure 3a), whereas at longer times recrystallization predominates (Figure 3b). This finding supports the interpretation of the two relaxation times τ_1 and τ_2 (Figure 2), both related to the events that progressively remove sample portions from the reversing melting/crystallization process: the contribution to the apparent reversing specific heat capacity connected to the relaxation time τ_1 is associated with partial melting and recrystallization/crystal perfection, whereas the contribution to τ_2 comes only from crystallization/crystal perfection processes. Similar results were found also for the quasi-isothermal measurement conducted at $T_0 = 489.6$ K.

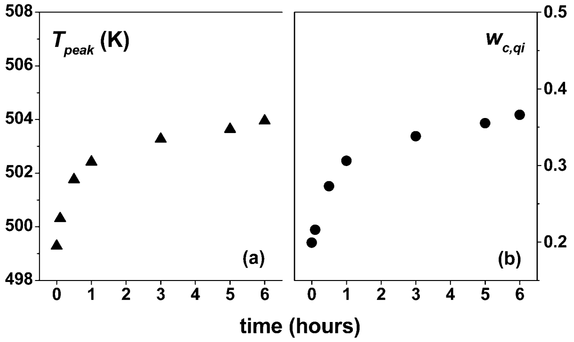

Figure 4. (a) Melting temperature and (b) crystalline fraction of PBT as a function of the time during the quasi-isothermal measurement at $T_0 = 498.4$ K.

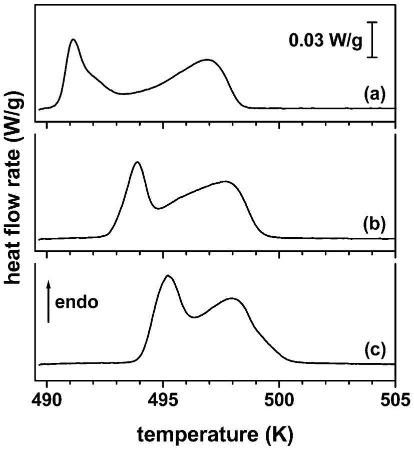

Figure 5. Standard DSC curves of PBT after (a) 6 min, (b) 3 h, and (c) 6 h of quasi-isothermal measurement at $T_0 = 489.6$ K; heating rate = 3 K/min.

The kinetics of reorganization processes that lead to the local equilibrium at the crystal−melt interface was also followed by monitoring the melting behavior after increasing times of the quasi-isothermal treatment. From integration of the DSC curves, the crystalline fraction at the end of the quasi-isothermal analyses ($w_{c,qi}$) was calculated, using for the fusion enthalpy of 100% crystalline PBT the literature value of 145 J/g.[21,22] The results, reported in Figure 4a,b for the quasi-isothermal modulations around 498.4 K, show that both the melting endotherm temperature (T_m) and the crystalline fraction increase with time of analysis, revealing the large occurrence of recrystallization and crystal perfection processes during the temperature modulations. These processes are very fast at the initial stages of the quasi-isothermal treatment and then proceed more slowly. It is worth noting that the considerable increase in T_m parallels the corresponding variation in $w_{c,qi}$. In fact, the T_m vs $w_{c,qi}$ plot (not shown) obtained for the data of Figure 4a,b is linear. This clarifies the type of crystallization occurring during the quasi-isothermal measurement. The increase in crystallinity with time of analysis has to be mainly ascribed to crystallization and annealing by progressive perfection of the crystals, being the fusion characterized by higher and higher melting temperature.

Similar results were obtained also for the modulation at $T_0 = 489.6$ K, as illustrated in the standard DSC curves of Figure 5, with shifts toward higher temperatures of both the endothermic peaks and an increase of

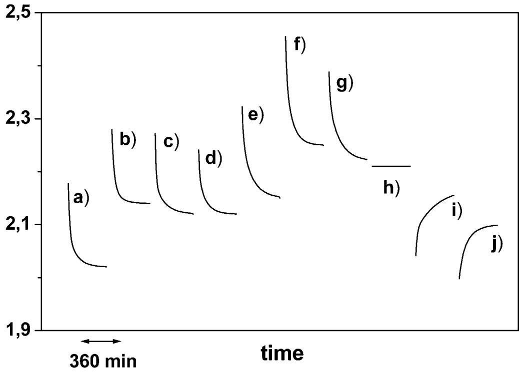

Figure 6. Time dependence of the apparent reversing specific heat capacity of PBT during quasi-isothermal measurements at (a) 488.4, (b) 490.4, (c) 491.4, (d) 493.4, (e) 495.4, (f) 498.4, (g) 499.4, (h) 500.4, (i) 501.4, and (j) 503.4 K. The data are from separate measurements and are collected in a single graph in order to compare the reversing c_p trends for different T_0's.

Table 1. Crystalline Fraction before and after the Quasi-Isothermal Treatments ($w_{c,0}$ and $w_{c,qi}$, Respectively), Equilibrium Reversing Heat Capacity ($c_{p,\infty}$), Baseline Heat Capacity ($c_{p,b}$), and Excess Heat Capacity ($c_{p,exc}$) Determined at the Indicated Temperatures of Quasi-Isothermal Analyses

T_0 (K)	$w_{c,0}$[a]	$w_{c,qi}$	$c_{p,\infty}$[b] [J/(g K)]	$c_{p,b}$[c] [J/(g K)]	$c_{p,exc}$ [J/(g K)]
487.4	0.307	0.351	2.00	1.956	0.04
488.4	0.305	0.359	2.02	1.958	0.06
489.6	0.298	0.367	2.06	1.959	0.10
490.4	0.292	0.380	2.14	1.960	0.18
491.4	0.292	0.385	2.12	1.962	0.16
492.4	0.299	0.384	2.11	1.965	0.15
493.4	0.300	0.383	2.12	1.967	0.15
494.4	0.298	0.380	2.13	1.970	0.16
495.4	0.288	0.368	2.15	1.974	0.18
498.0	0.212	0.360	2.24	1.982	0.26
498.4	0.188	0.350	2.25	1.984	0.27
499.4	0.117	0.318	2.22	1.990	0.23
500.4	0.049	0.266	2.21	1.998	0.21
501.4	0.008	0.133	2.17	2.015	0.16
502.4	0	0.087	2.11	2.022	0.09
503.4	0	0.057	2.10	2.028	0.07

[a] Calculated from the partial areas of the $c_{p,total}$ curve (Figure 1). [b] Error: ±0.03 [J/(g K)]. [c] $c_{p,b} = w_{c,qi}c_{p,c}+(1 - w_{c,qi})c_{p,a}$ where $c_{p,c}$ and $c_{p,a}$ are the crystalline and amorphous heat capacities, respectively, taken from ATHAS data bank.[22]

the crystalline fraction. Figure 5 shows that a prolonged permanence at the temperature corresponding to the lower fusion peak (489.4 K) produces recrystallization into structures which can be further perfected, since the DSC plot after the quasi-isothermal treatment still presents a double endotherm.

Last, the effect of the small temperature oscillations on the recrystallization/crystal perfection/annealing processes was evaluated by comparison with simple isothermal treatments conducted in the conventional DSC mode. The crystallinity, calculated after quasi-isothermal analyses of different duration at 498.4 K, was always found perfectly coincident with the crystallinity measured after isothermal treatments of the same time, but without modulation. Thus, it was inferred that the temperature modulation around T_0 does not influence the extent of the total recrystallization process of PBT, in agreement with results presented in ref 16. Nevertheless, it is worth emphasizing that information gained from quasi-isothermal TMDSC runs is more comprehensive because this technique allows to discriminate between exothermic and endothermic events, which cannot be identified by a conventional DSC scan if they occur simultaneously.

Quasi-Isothermal Analyses over the Complete Melting Range. Besides the experiments conducted at the temperatures corresponding to the two maxima of the reversing heat capacity of Figure 1, further quasi-isothermal analyses were performed at increments of 1.0 K, starting from 487.4 K. The time of the measurements was 6 h, excluding those in the T_0 range 501.4–503.4 K, whose duration was raised to 7 h because of the slower reorganization kinetics. Results of these measurements are summarized in Figure 6. They indicate that the structural reorganizations of the crystal phase in PBT are strongly affected by the temperature of analysis. Below 500 K the apparent reversing specific heat capacity plotted vs time displays the commonly observed double-exponential decay.[4] When PBT is analyzed at 500.4 K, the apparent reversing c_p remains practically constant at a value of 2.21 J/(g K) during the whole measurement. This value is higher than the baseline c_p of liquid PBT, determined in absence of thermal events, similarly to the trend reported in the literature for a poly(ether–amide) segmented copolymer.[18] For quasi-isothermal analyses carried out at higher temperatures, the apparent reversing c_p shows a quite unusual trend, increasing with measurement time.

As already evidenced, a complex process is involved in the decrease of the apparent reversing heat capacity with time, including both fusion and recrystallization and/or crystal perfection. A fully melted molecule or molecular segment longer than a critical length is removed from the reversing melting if the supercooling required for the recrystallization is not achieved during the modulation cycle.[4] Similarly, since the thermal stability of a recrystallized structure is higher than that of the original crystals, each more perfect crystal has a higher melting temperature (see Figures 4 and 5) and is thus removed from the successive melting cycle, so that the crystal fraction that participates in the melting process reduces progressively. This results in a corresponding decrease of latent heat contributions to the apparent reversing c_p.

Different is the case of quasi-isothermal analyses performed at temperatures ranging from 501.4 to 503.4 K. Measurements conducted at these temperatures start with an apparently completely melted (or almost completely melted) PBT sample that recrystallizes during the quasi-isothermal modulation around T_0. Recrystallization at high temperatures, starting from a melted sample, was also observed in poly(ethylene terephthalate).[24] Recrystallization of PBT immediately occurs at the beginning of the quasi-isothermal analysis, continuously adding new crystals that participate in the reversing melting process: the effect is a continuous increase in the measured reversing c_p. At intermediate temperatures (500.4 K), fusion, recrystallization, and crystal-perfection processes are counterbalanced during the 6 h of experimental measurement, which results in a constant apparent reversing c_p.

The crystalline fractions before and after the quasi-isothermal treatments ($w_{c,0}$ and $w_{c,qi}$, respectively) are presented in Table 1. As already observed for the measurements at 489.6 and 498.4 K (Figures 4 and 5), the increase of the crystalline fraction is considerable for quasi-isothermal treatment performed in the whole melting range. This large increase in crystallinity might be favored by a lower molecular mass resulting from chain degradation, especially at high T_0: a low molecular mass increases chain mobility, which, in turn, may favor formation of crystals in the presence of proper nuclei. Literature data indicate that PBT degrades upon prolonged exposure at temperatures of 513.2 K and above.[25] Degradation involves chain scission via elimination of butadiene, and after 6 h of permanence at 513.2 K, the average molecular weight approximately reduces to a half. No literature data were found on degradation of PBT at the temperatures where quasi-isothermal measurements were conducted in this study. Ester interchange reactions at high T_0 were also found to favor recrystallization and crystal perfection in the lower homologue of PBT, poly(ethylene terephthalate): because of the break of main-chain bonds outside the crystals, the mobility of the polymer segments comes out enhanced and the effects of the constraints, such as entanglements and tie chains, reduced.[26,27]

To test whether the above chemical reactions can modify the reorganization process of PBT crystals monitored by the quasi-isothermal measurements, a comparison was made at $T_0 = 495.4$ K between a fresh sample and a sample previously maintained for a prolonged time (6 h) at 508.2 K. The apparent reversing c_p values were found perfectly coincident for both samples during the whole time of analysis; thus, the effect of degradation on the heat capacity increase at high T_0 was considered minor.

As already pointed out, when quasi-isothermal analyses are performed at the highest temperatures of analyses (502.4 and 503.4 K), the prolonged permanence around the base temperature of modulation T_0 favors recrystallization of the just melted chains. Because of software limitations of the TMDSC apparatus used,[28] reversing c_p data cannot be monitored during the first three modulation cycles, so the kinetics of crystal reorganization, as illustrated in Figure 2, is lost for the first 6 min of each quasi-isothermal analysis. In this way, it is not possible to determine whether the initial c_p was that corresponding to the baseline value of liquid PBT or if some thermal events occurred at the very early stages of the quasi-isothermal analysis. Even if the crystal/amorphous ratio at the beginning of the quasi-isothermal measurements is evident from Figure 1, to check it in quasi-isothermal conditions, a temperature program operating in the conventional DSC mode was used to monitor the variation in reversing c_p in the initial stages of the reorganization process. The program was made of 12 linear segments, corresponding to the maximum number of steps allowed by the software[28] and forming a sawtooth temperature profile. The experimental data were analyzed with the common TMDSC procedure summarized in eq 1. It was found that, when the quasi-isothermal modulation started, the initial c_p at time $t = 0$ min was coincident, within experimental uncertainties, with the baseline c_p value of pure liquid PBT,[22] indicating that crystal reorganization at temperatures above 501 K starts from a liquid PBT sample. However, the melt phase of PBT is probably not completely disordered, as some memories of partially ordered chain portions are expected to remain, which clearly helps the onset of phase transformation.[29,30]

The various recrystallization, crystal-perfection, and melting processes visualized in Figure 6 point toward a reversible steady state, which may be a true local equilibrium between the metastable crystals and the surrounding melt. This local equilibrium, often addressed as "reversible melting", strongly depends on the temperature of analysis. The amount of reversible melting can be estimated via the excess specific heat capacity ($c_{p,\mathrm{exc}}$), calculated as the difference between the equilibrium reversing specific heat capacity ($c_{p,\infty}$), determined with the quasi-isothermal measurements, and the baseline value ($c_{p,\mathrm{b}}$), taken from the ATHAS data bank.[22] The value of baseline heat capacity, i.e., the heat capacity without latent heat contributions, was computed by taking into account the measured crystalline fraction at the end of the quasi-isothermal analyses ($w_{\mathrm{c,qi}}$), reported in Table 1, under the hypothesis that a two-phase model is valid for PBT at the temperatures under investigation. This model, which considers only crystalline and amorphous moieties and neglects the presence of an interphase between the crystals and the surrounding melt, was chosen because the devitrification process of the rigid amorphous fraction of PBT has not been completely identified, which implies that the physical state of the interphase at the temperatures of analysis is at present not known.[4,21] However, the error introduced by this approximation should be small because the baseline heat capacities of liquid and solid PBT are very close in the investigated temperature range.[22] The values of the specific heat capacities $c_{p,\infty}$, $c_{p,\mathrm{b}}$, and $c_{p,\mathrm{exc}}$ as a function of the quasi-isothermal modulation temperature are reported in Table 1. The equilibrium reversing specific heat capacities $c_{p,\infty}$ is compared in Figure 7 with the solid and liquid specific heat capacities from ATHAS data bank.[22] The occurrence of endothermic and exothermic processes giving rise to reversible melting is evidenced by the values of $c_{p,\infty}$, higher than the liquid specific heat capacity. On the contrary, the values of the baseline $c_{p,\mathrm{b}}$, being characterized by no latent heat contributions, fall within the solid and the liquid specific heat capacities. It is worth noting that the $c_{p,\infty}$ curve presents two maxima, centered around 490 and 498 K, i.e., the temperatures where the peaks of the heat capacities curves are located (see Figure 1).

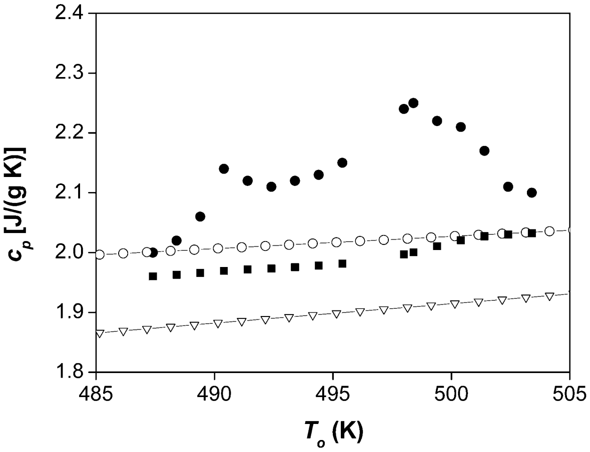

Figure 7. Equilibrium reversing specific heat capacity ($c_{p,\infty}$, ●) and baseline specific heat capacity ($c_{p,\mathrm{b}}$, ■) as a function of the quasi-isothermal modulation temperature T_0. The specific heat capacity of the solid and liquid PBT (▽ and ○, respectively) are from the ATHAS data bank.[22]

The fusion behavior of PBT after the quasi-isothermal analyses at various temperatures is exhibited in Figure 8, which shows the dependence of the endothermic melting peaks (T_{peak}) on the base temperature of the

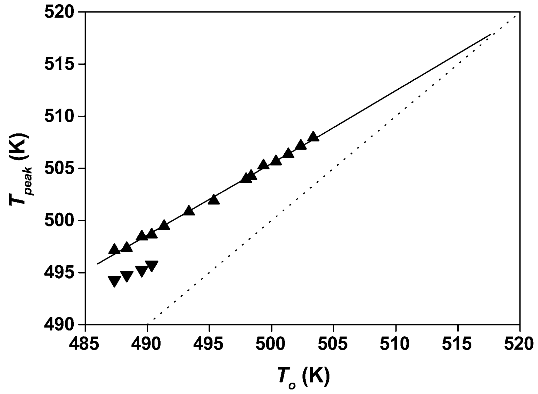

Figure 8. Melting temperatures (T_{peak}) of PBT after quasi-isothermal measurements as a function of the quasi-isothermal modulation temperature T_0: (▼) lower temperature melting peak; (▲) higher temperature melting peak. The dashed line ($T_{\mathrm{peak}} = T_0$) is drawn for the Hoffman−Week extrapolation.[31]

quasi-isothermal modulations (T_0). Two linear and approximately parallel trends of the melting temperatures are evident, with double endotherms being observed after the quasi-isothermal treatments in the T_0 range 487.4−490.4 K. Extrapolation of melting data according to Hoffman−Weeks procedure[31] leads to an apparent equilibrium melting point of 517.4 K.

It needs to be underlined that melting point data reported in Figure 8 were collected after 6 or 7 h of quasi-isothermal analysis. The measured melting temperature is strongly affected by annealing time, as illustrated in Figures 4 and 5, which implies that prolonging the time of quasi-isothermal experiments would lead to an increased fusion temperature, which, in turn, would result in a higher apparent equilibrium melting point. Also, the scanning rate used for the DSC analyses after the quasi-isothermal treatments strongly affects the reorganization processes,[1] and in PBT this seems to prevail on the effects of prolonged permanence at temperatures below 490 K. In fact, in the DSC curves determined after prolonged permanence at $T_0 < 490$ K (scanning rate = 3 K/min), the lower melting endotherm is located at temperatures slightly lower than that of the PBT sample only crystallized at 473 K for 30 min (scanning rate = 0.5 K/min) (see Figures 8 and 1). The most reliable value of $T_{\mathrm{m}}^{\mathrm{o}}$ for PBT is 523.2 K,[32] as detailed in ref 33, which presents a critical analysis of $T_{\mathrm{m}}^{\mathrm{o}}$ values of PBT reported in the literature; hence, the extrapolated value of $T_{\mathrm{m}}^{\mathrm{o}} = 517.4$ K does not need to be taken as the real equilibrium melting temperature of poly(butylene terephthalate).

The two linear trends of the fusion endotherms with the temperature of the quasi-isothermal analysis, shown in Figure 8, might be correlated to different morphologies of the PBT crystallites on a nanometer scale. From literature data it is well-known that the double melting behavior of PBT does not involve recrystallization into a different crystal modification and seems not affected by variations in crystal morphology, at least at the microscopic level.[34,35] In fact, it has been found that PBT presents different spherulitic morphologies,[36] but this does not affect the melting behavior.[37] Moreover, during a heating scan, the spherulitic superstructures formed during isothermal crystallization at 473 K was found to remain unchanged until complete fusion.[37] However, it is undisputed that the two different peaks originate from two different spatial organizations of PBT chains, which might be linked to different physical states of the melt−crystal interface.

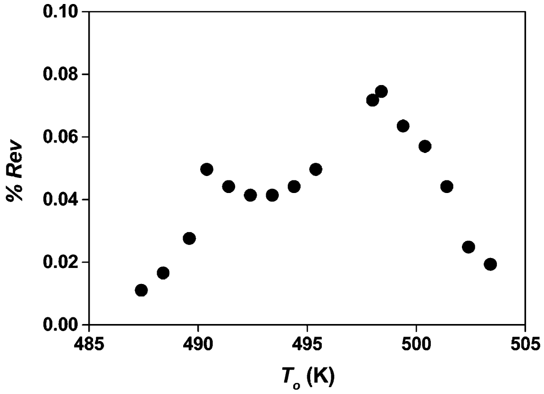

Figure 9. Reversibility degree of the melting/crystallization process (% Rev) in PBT as a function of the quasi-isothermal modulation temperature T_0.

In this connection it is useful to consider the dependence on T_0 of the fraction of crystal population that undergoes reversible melting (% Rev), quantified as[13]

$$\% \ \mathrm{Rev} = \frac{2A_T c_{p,\mathrm{exc}}}{\Delta H_{\mathrm{m}}^{\mathrm{o}}} \times 100 \qquad (2)$$

where $\Delta H_{\mathrm{m}}^{\mathrm{o}}$ is the enthalpy of fusion computed for 100% crystallinity and A_T is the modulation amplitude. Being % Rev derived from the equilibrium reversing specific heat capacity $c_{p,\infty}$, also the % Rev vs T_0 curve presents two maxima centered around 490 and 498 K, as shown in Figure 9.

It was noted above that a prolonged permanence at the temperature corresponding to the lower fusion peak (489.4 K) produces recrystallization into structures which are still defective, as evidenced by the double endotherm in the DSC curves obtained after the quasi-isothermal treatments (Figures 5 and 8). The crystallites developed at $T_0 \leq 490$ K are kinetically favored, but highly metastable, and reorganization into more stable structures seems impossible at these temperatures and attainable only upon heating above 490 K. This may be linked to the spatial arrangement of the amorphous PBT chains.

In semicrystalline PBT, a large fraction of the noncrystalline material is rigid amorphous.[21] Partial devitrification of the RAP (rigid amorphous phase), involving only a limited fraction of the total RAP, occurs in the temperature range 313−322 K, depending on crystallization conditions.[21] The temperature at which the remaining rigid amorphous fraction devitrifies has not been established yet but may be located in the temperature range where fusion occurs. It is likely that below 490 K the amorphous phase is not totally mobile and that, on the contrary, devitrification is complete in proximity of the temperature of the second melting peak. Thus, the distribution and the organization of the amorphous phase might lead to development of structures of different thermal stability.

The percentage of reversible melting is obviously connected to the crystallinity degree $w_{c,\mathrm{qi}}$[23,38] that, for the analyzed PBT, presents a maximum as a function of the base temperature T_0, as shown in Table 1. Taking into account that the reversible melting process can occur only if the amorphous segment chains in proximity of the crystal/melt interface have sufficient mobility,

% Rev may be linked also to the degree of devitrification, which might be an increasing quantity in this temperature range. On the basis of these considerations, the % Rev trend with two local maxima, shown in Figure 9, could be explained. Further investigations are in progress in order to find a possible correlation between the double melting behavior of PBT and the fraction of rigid amorphous phase.

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