

Morphological analysis of poly(butylene terephthalate) spherulites during fusion

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Summary

A detailed morphological analysis of the melting process of poly(butylene terephthalate) (PBT) is presented. Investigations were conducted by polarizing optical microscopy, coupling the measurement of depolarized light intensity with examination of morphology of PBT spherulites during their fusion. These analyses allowed to prove that the spherulitic superstructure of PBT developed upon isothermal crystallization from the melt does not vary with temperature until complete melting takes place, despite the large reorganization involved in the fusion process. It is thus shown that the double melting behavior commonly observed in PBT does not arise from the presence of various spherulitic morphologies with different thermal stabilities, and the structural changes caused by the reorganization processes do not involve variations in the spherulitic morphology. The recrystallization of PBT above the apparent melting point was also analyzed, and the role of memory effects of crystalline precursors remaining in the melt was discussed.

Keywords

PBT, melting, recrystallization, birefringence, morphology, depolarized light intensity

Introduction

Experimental studies of polymer melting are generally conducted in conditions far from thermodynamic equilibrium, since the large specific surface area of polymeric nanocrystals, coupled with their high number of defects, induces fusion to occur at temperatures much lower than the thermodynamic melting point [1]. Upon heating, the polymeric crystal phase can undergo complex structural reorganizations, including annealing, recrystallization, crystal perfection and secondary crystallization, all overlapping pure melting [2]. These reorganization processes are associated with thermal events, and are generally monitored by evaluating the heat absorbed and/or evolved by the sample under analysis, using differential scanning calorimetry, either in the conventional mode (DSC), or with temperature-modulation (TMDSC) [3–4].

A detailed calorimetric analysis of the melting process of poly(butylene terephthalate) (PBT), presented in Ref. 5-7, allowed to identify and quantify the structural reorganizations of the crystal phase that overlap main melting. It was found that the multiple melting behavior commonly observed in PBT is the sum of simultaneous events of fusion of small and defective crystals and of their immediate recrystallization into more stable structures. Moreover, melting of PBT is largely irreversible, and only a small fraction of the overall crystal population, strongly depending on temperature, undergoes reversible melting. The total latent heat involved in the various reorganization processes of the crystal phase decreases with time when quasi-isothermal analyses are conducted at temperatures below 500 K, as a result of partial fusion, crystal perfection and recrystallization, which simultaneously occur and overlap. Above 500 K, instead, an increase with time of the apparent reversing heat capacity was observed, revealing the occurrence of recrystallization processes starting from an apparently melted PBT.

To complete the investigation of PBT melting, morphological analyses were conducted by polarizing optical microscopy, and results detailed in this contribution. Reasoning for the investigation of morphology of PBT during melting arises from the observation of different types of spherulites in PBT, depending on crystallization conditions [8-10]. Stein and Misra first showed the existence of different arrangements of the planes of polarization of PBT crystals in dependence of crystallization conditions: PBT forms "unusual" spherulites with optical axes laying at an angle of about 45° to the spherulite radius, as well as "usual" spherulites with optical axes either along or perpendicular to the spherulite radius and a maltese cross along the polar direction when analyzed under a polarizing optical microscopy [8]. The two types of spherulitic morphologies derive from different preferred radial orientations of PBT crystallites: in the usual spherulites the $(\bar{2}10)$ plane is oriented in the radial direction, whereas in the unusual ones the $(\bar{1}11)$ direction is radial [11]. Mixed-type spherulites, showing diffraction patterns in multiple directions, are also often encountered in PBT, and arise from superposition of the different crystal orientations within the same spherulite. Moreover, when PBT is crystallized from the melt at temperatures above 483 K, crystallites with a roughly spherical shape and less defined borders form, and their extinction patterns cannot be recognized within any particular direction respect to the polarizer and the analyzer, as the dark and bright areas alternate without a defined regularity [8,10].

The presence of different spherulite types in PBT has been sometimes correlated with its multiple melting behavior [8-9], although criticism to this interpretation has also appeared [12]. Criticism was based on the observation of multiple melting in a PBT sample that was mostly made of usual spherulites, but the hypotheses put forward in Ref. 12 were not proven. Conversely, the experimental evidences presented in this contribution demonstrate that the multiple melting behavior of PBT is independent of the type of spherulitic morphology developed upon primary crystallization, and that the overall spherulitic superstructure remains unchanged in spite of the large reorganizations of the crystal phase, until complete fusion occurs. These reorganization processes, quantified in Ref. 7 using TMDSC analysis, have also been monitored by measurement of depolarized light intensity, as described in this article.

Experimental Part

Material

Poly(butylene terephthalate) (PBT) of molar mass $M_n=44,000$ g/mol and $M_w=81,000$ g/mol, was purchased from Sigma-Aldrich Corp. Detailed analyses on its thermal properties were reported in Ref. 6-7,10. The sample chips were compression-molded with a Carver Laboratory Press at a temperature of 523 K for 3 minutes, 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.

Optical Microscopy

Melting kinetics of PBT was investigated by optical microscopy, using a Zeiss polarizing microscope equipped with a Linkam TMHS 600 hot stage. An automatic exposure apparatus, mounted on the optical microscope, was used to measure the intensity of light transmitted between crossed polars. The time to exposure (t_e), needed to impress a film of a given sensitivity in a MC-100 camera, was detected by an electronic digital display, and recorded as a function of temperature or time.

Thermal treatments

A small piece of PBT was squeezed between two microscope slides, then inserted in the hot stage. The thickness of the squeezed sample was lower than 10 μm . Before the morphological analyses, the samples were subjected to the same thermal treatment used for the DSC and TMDSC measurements reported in Ref. 6 and 7: Each PBT sample was heated from 303 to 523 K, kept at this temperature for 3 min to allow complete melting, then quickly cooled to 473 K and allowed to crystallize for 30 minutes. After isothermal crystallization, the sample was heated at a rate of 0.5 K/min until fusion occurred. Morphology development was recorded during the final heating at 0.5 K/min.

Morphological evolution of isothermally crystallized PBT was also monitored during prolonged permanence at high temperatures. This was performed after isothermal crystallization at 473 K for 30 min, followed by a heating scan at a rate of 0.5 K/min (as before). When the temperature reached 503 K, quasi-isothermal sawtooth modulation started, with temperature oscillating between 502 and 503 K, using heating and cooling rates of 1 K/min ($A_T=0.5$ K; $p=120$ s).

Dry nitrogen was used as purge gas in the hot stage during all measurements and thermal treatments.

Results and Discussion

Figure 1 reports the optical micrograph of a typical PBT sample isothermally crystallized at 473 K for 30 min, showing a spherulitic superstructure. The spherulites are prevalently of the mixed type [9], with extinction patterns in multiple directions, due to superposition of extinction patterns at 0 and 45°, as common for crystallization conducted at this temperature [10]. A few unusual spherulites can also be distinguished [10]. This PBT sample was heated at a rate of 0.5 K/min, and optical

micrographs were taken at various temperatures during the heating scan, as illustrated in Figure 2. Analysis of the optical micrographs at the various temperatures shows that the multiple extinction patterns of PBT spherulites are unaffected by the raising temperature until complete fusion, and only a variation in the intensity of depolarized light that follows the temperature changes can be observed.

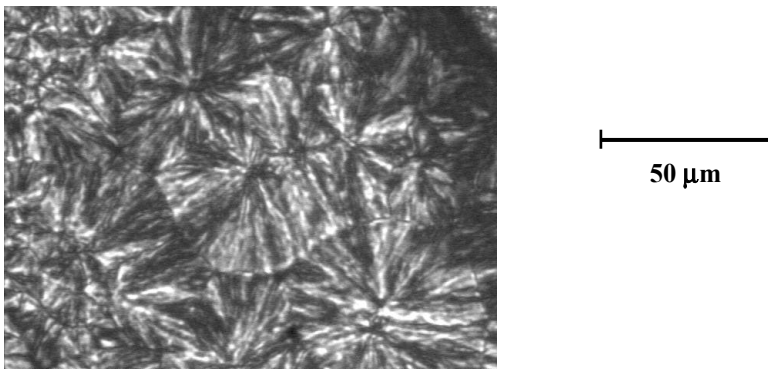


Figure 1. Optical micrograph (crossed polars) of PBT after isothermal crystallization at 473 K for 30 min.

The double melting behavior of PBT has been sometimes correlated to the diverse thermal stability of its spherulites. Ludwig and Eyerer derived different melting enthalpies associated with usual and unusual spherulites (60 J/g and 48 J/g, respectively), and attributed the higher endotherm to fusion of the unusual type, and the lower endotherm to melting of the usual spherulites [9]. The opposite assignment was instead reported by Stein and Misra [8]. Conversely, Yeh and Runt attributed both melting endotherms to fusion of the usual spherulites. Our analysis of the evolution of the morphology of PBT spherulites during a heating scan, reported in Figures 1 and 2, proves instead that the spherulitic superstructure developed upon isothermal crystallization (mixed type, in the present case) does not vary during the whole heating scan until fusion. No variation of diffraction patterns can be observed. Both the patterns oriented at 45° , and those oriented in the polars directions, typical of unusual and usual spherulites respectively, whose superposition produces the mixed-type spherulites illustrated in Figures 1 and 2, are unaffected by the temperature variation, and their birefringence disappears as a whole when the melting point is approached. The observed decrease of birefringence with temperature, due to fusion, simultaneously occurs in the various directions respect to the polars, which proves that the usual and unusual spherulites have the same thermal stability, and that, during fusion, no conversion of a less stable spherulitic morphology into the other one takes place.

The variation in the intensity of light transmitted between the crossed polars by the birefringent PBT spherulites was monitored as a function of temperature, in order to gain information on melting behavior. The use of depolarized light transmission is often used as a tool for the study of crystallization kinetics [13-15], or to detect melting temperatures of crystallized polymers [16], but to our knowledge no report

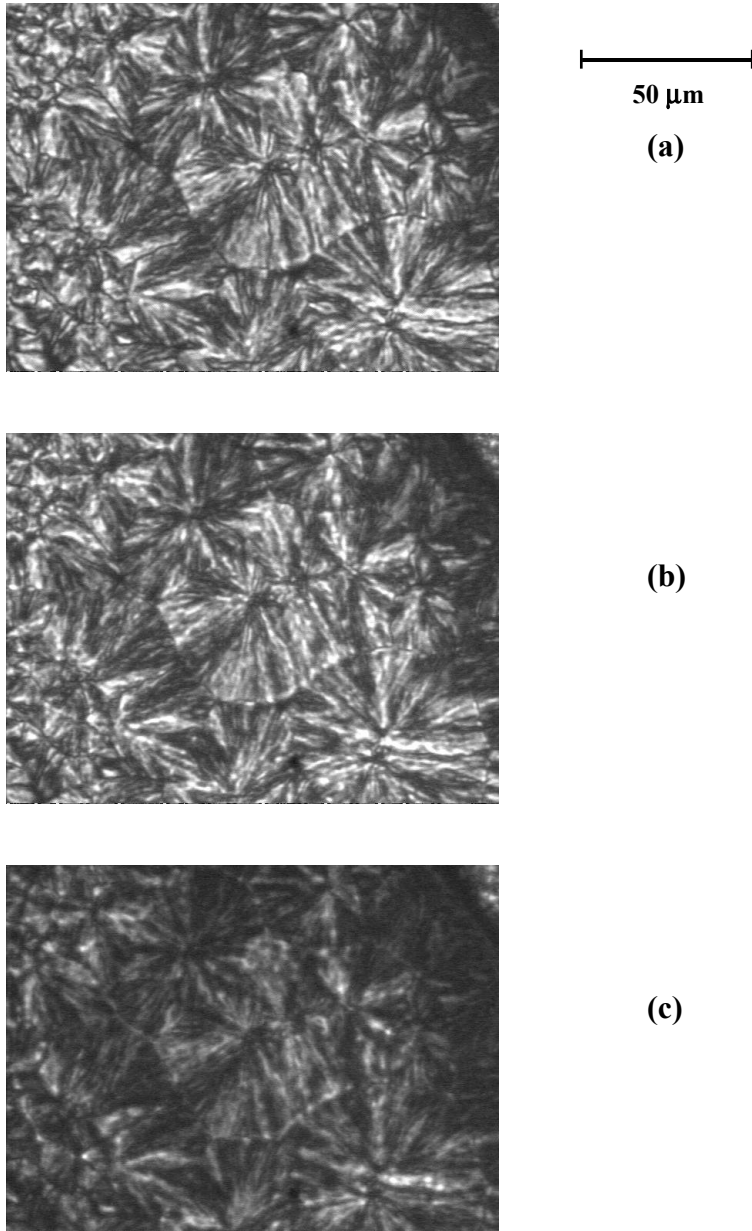


Figure 2. Optical micrographs (crossed polars) of PBT isothermally crystallized at 473 K for 30 min, then heated at 0.5 K/min. Micrographs were taken at various temperatures during the heating at 0.5 K/min: (a) 483 K; (b) 493 K; (c) 502 K.

exists on the use of depolarized light intensity to follow melting kinetics. It is generally assumed that, at any time, the intensity of depolarized light increases with the fraction of crystallized material (w_c) [17], which allows to monitor phase change

kinetics as a function of temperature and/or time. Unfortunately, the detected light intensity depends not only on the light source, the glass slide, the optics, and the detection system, all parameters that can be easily kept constant during a series of experiments, but also on sample thickness, which is a very difficult parameter to control in very thin samples (generally below 10 μm). For these reasons it is not possible to obtain quantitative evaluations of melting kinetics by analysis of the depolarized light transmission intensity [17], but only to derive qualitative information that can complement the DSC and TMDSC analyses reported in Ref. 5-7.

Figure 3-a reports the reciprocal of the exposure time necessary for a photomicrograph ($1/t_e$), which depends on the crystalline fraction of the material (w_c), as it varies during the heating scan at 0.5 K/min. The trend of $1/t_e$ with temperature (T) is very similar to the w_c vs. T plot obtained by DSC measurements, reported in Ref. 6 and repeated in Figure 3-b for comparison purposes. Both figures 3-a and 3-b reveal an overall decrease in crystallinity of PBT with temperature. This decrease begins together with the onset of the heating scan, and is followed by a shallow minimum around 490 K, a slight increase in w_c , and finally by a drastic decrease of w_c down to a value of zero crystallinity when all the material is melted, thus evidencing a double melting transition. Combined analysis of Figures 2 and 3 confirms that the double melting behavior of PBT is independent of the presence of different types of spherulites. It arises from fusion of smaller and/or more defective crystals and their recrystallization during the heating scan, as shown by TMDSC [6], and the sequence of optical micrographs exhibited in Figure 2 proves that the different radial orientations of PBT crystallites do not affect the final melting temperature.

The very good agreement between the qualitative data of Figure 3-a with the quantitative data illustrated in Figure 3-b, shows that the analysis of depolarized light intensity can be successfully applied to follow melting kinetics of polymers. Hence, this method was also used to monitor the variation in crystallinity of PBT during prolonged permanence at high temperatures. This was performed by modulating around a base temperature, in order to parallel the quasi-isothermal TMDSC analyses described in Ref. 7, where recrystallization of PBT above the melting temperature was reported. Results are illustrated in Figure 4, for a quasi-isothermal modulation around 502-503 K. At the beginning of the quasi-isothermal analysis, the PBT sample is in the melt state [7], although some residual birefringence remains. Crystallinity rapidly increases as soon as the heating scan stops and the temperature starts to modulate between 502 and 503 K, indicating large and immediate recrystallization of the almost melted sample. The insert in Figure 4 shows that recrystallization proceeds during both heating and cooling steps between 502 and 503 K, but with different kinetics: recrystallization is rapid during the cooling cycles, and proceeds more slowly during the heating segments of temperature modulation.

Since the kinetics of fusion/recrystallization/annealing processes is largely affected by the rate of temperature variation, the continuous competition among fusion, recrystallization and annealing leads fusion to prevail around 500 K when PBT is heated at rate of 0.5 K/min, as a result of the constant temperature increase (see Figure 3). Conversely, when temperature is quasi-isothermally modulated around 502-503 K, recrystallization and crystal perfection processes are favored, resulting in a rapid increase of the crystal fraction in spite of the high temperatures of analysis. This allows fast recrystallization of the just melted chains at high temperatures, even above the apparent melting point.

The recrystallization process of PBT at high temperature was also followed by taking optical micrographs of PBT spherulites at various times of permanence at 503 K. Results are exhibited in Figure 5, and refer to the same PBT sample shown in

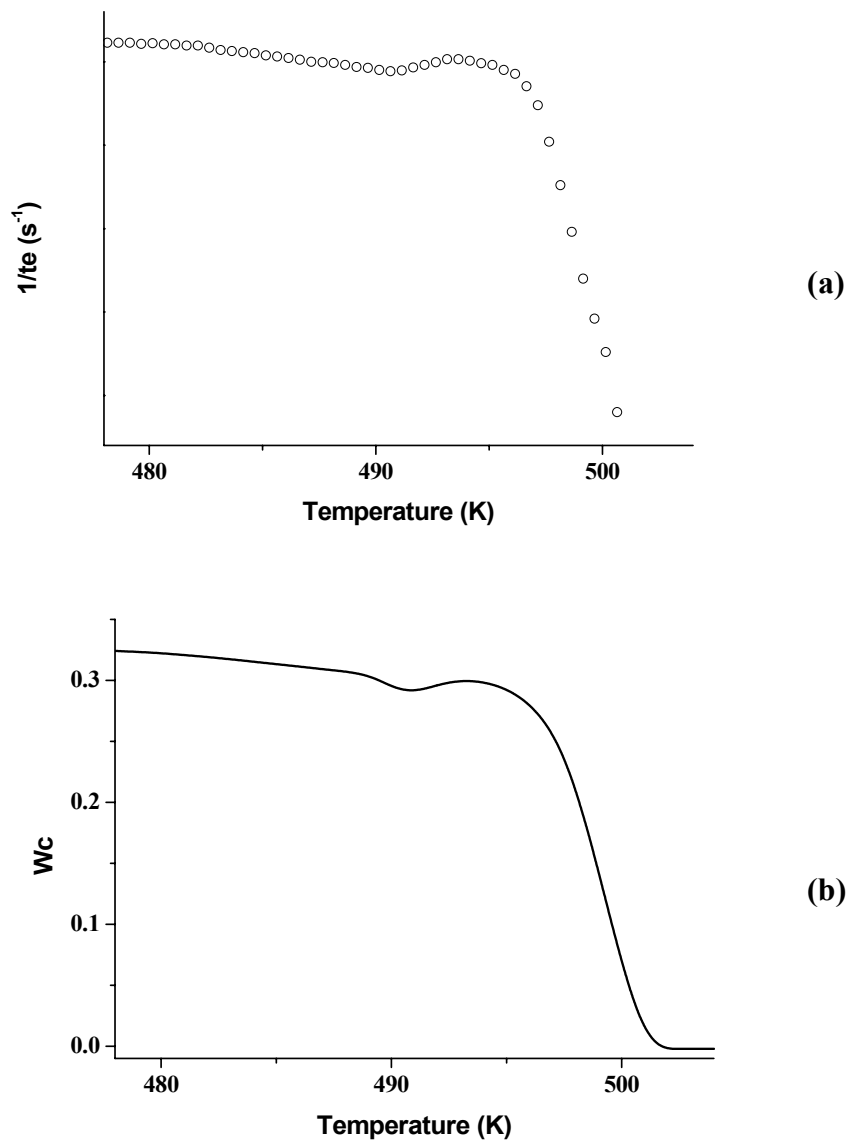


Figure 3. (a) Reciprocal of the exposure time ($1/t_e$) as a function of temperature, recorded during heating at 0.5 K/min of a PBT sample isothermally crystallized at 473 K for 30 min. (b) Temperature dependence of the enthalpy-based crystallinity (w_c) of a PBT sample isothermally crystallized at 473 K for 30 min (data taken from Ref. 6).

Figures 1 and 2. Birefringence of PBT spherulites rapidly increases with time, following the occurrence of large recrystallization. Besides the increase in birefringence, no other variation in the spherulitic morphology can be observed, and the spherulitic microstructure of the recrystallized material results identical to that of the original sample crystallized at 473 K, differing only in the intensity of depolarized light.

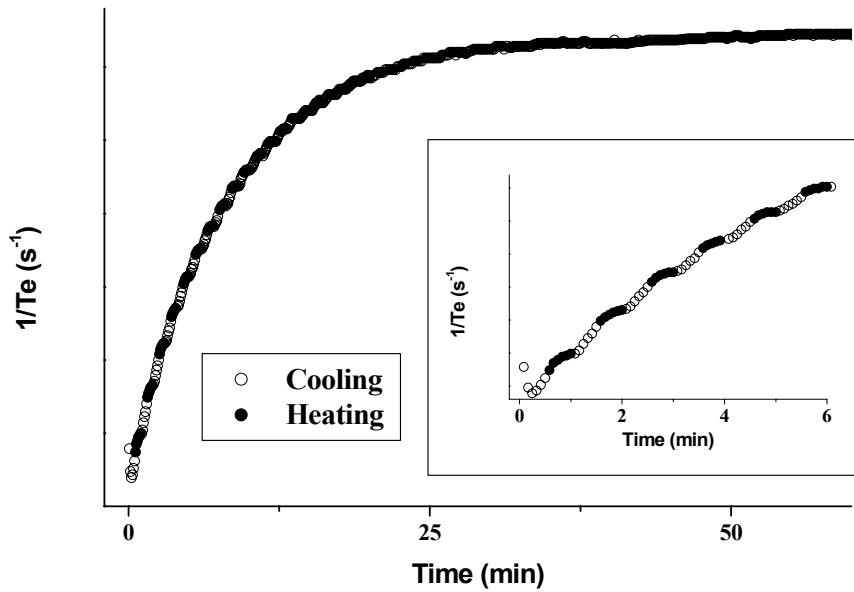


Figure 4. Reciprocal of the exposure time ($1/t_e$) as a function of time during quasi-isothermal modulation between 502 and 503 K of a PBT sample isothermally crystallized at 473 K for 30 min, then heated at 0.5 K/min to the quasi-isothermal temperature; $A_T = 0.5$ K; $p = 120$ min.

In Ref. 7 it was shown that, at temperatures higher than 500 K, the large recrystallization observed during quasi-isothermal modulations starts from an apparently completed melted PBT sample. This was based on the observation that the apparent reversing heat capacity (C_p) at the beginning of the quasi-isothermal analyses coincides with the thermodynamic C_p of the pure liquid. Despite being in the liquid state, the possible role of residual crystal memories was hypothesized. From comparison of Figure 5 with Figures 1 and 2, it can be inferred that memory effects play a fundamental role in recrystallization of the apparently melted PBT chains. The newly formed PBT spherulites illustrated in Figure 5 grow exactly in the same position, and with the same appearance of the original spherulites of Figures 1 and 2, which refer to PBT before and during the fusion process. The recrystallization process of PBT spherulites is thus facilitated by the small chain aggregates remaining in the liquid phase, that act as precursors for crystal growth.

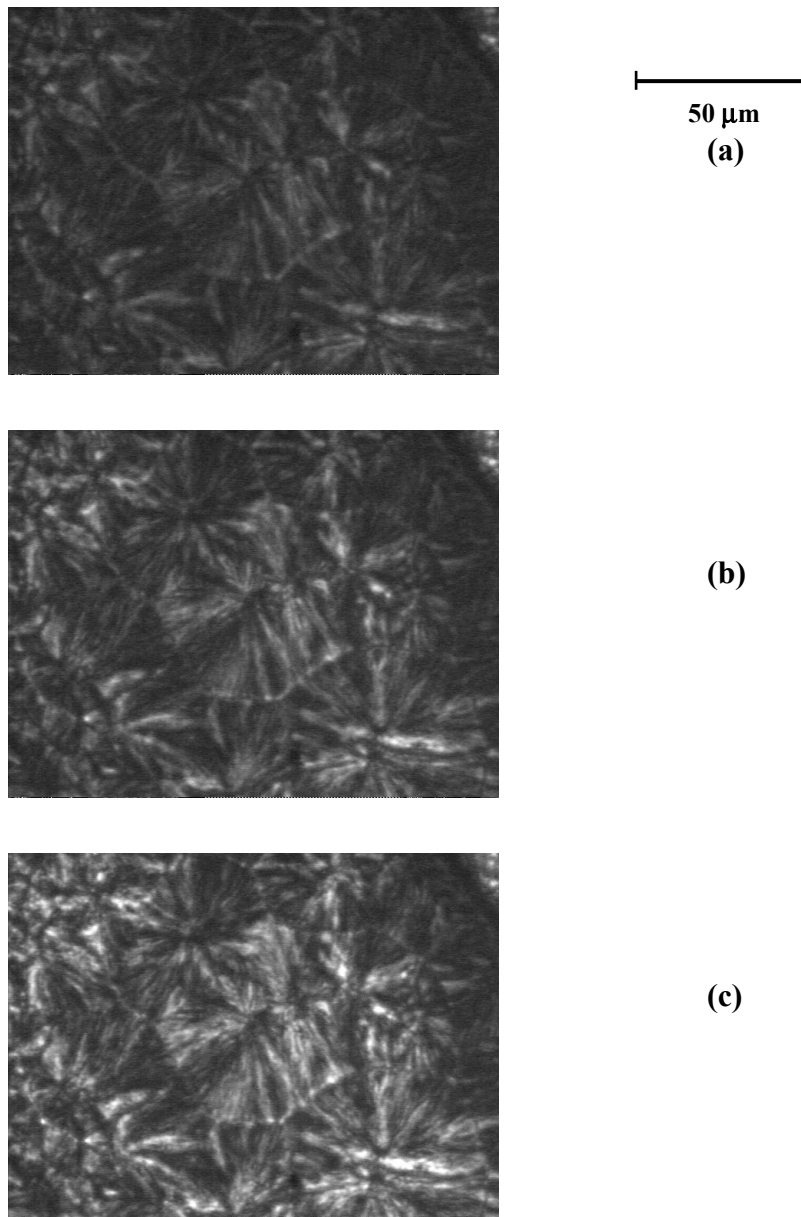


Figure 5. Optical micrographs (crossed polars) of PBT isothermally crystallized at 473 K for 30 min, then heated to 503 K at a rate of 0.5 K/min. Micrographs illustrate recrystallization at 503 K: (a) after 30 s; (b) after 15 min; (c) after 90 min.

Conclusions

The reported results demonstrate that the analysis of depolarized light intensity can be successfully used to monitor the melting process of polymers. Even if it cannot

provide quantitative information, measurement of depolarized light intensity of a birefringent sample has the advantage of providing the simultaneous observation of morphology development and phase change kinetics. Application of this technique to fusion of PBT spherulites allowed to demonstrate that the double melting behavior of poly(butylene terephthalate) is solely attributable to repeated fusion/recrystallization processes, and does not arise from different initial morphologies developed upon primary crystallization, nor from variations in the spherulitic morphology occurring during the heating scan that leads to fusion.

The recrystallization above the melting point of an apparently liquid PBT, discussed in Ref. 7, was proven to start from small chain aggregates that facilitate reordering of PBT chains, and does not produce visible variations in the spherulitic morphology.

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