

Study of Melting Processes in Semicrystalline Polymers Using a Combination of Ultrafast Chip Calorimetry and Nanofocus Synchrotron X-Ray Diffraction

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Abstract—This work is devoted to the development and application of a new experimental method that combines in situ ultrafast calorimetry on a chip with nanofocus synchrotron X-ray diffraction. In the present work, this method is used to study the melting mechanisms of samples of semicrystalline polymers with the mass of a few tens of nanograms. Such studies are relevant when working with materials that are characterized by complex phase behavior, for example, prone to transitions into metastable states or demonstrating fast processes of structural adjustment during thermal treatment.

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INTRODUCTION

The development of new methods of physical and chemical analysis of samples weighing a few nanograms is an urgent task in the applied fields of science such as pharmacy, development of new explosives, and others. For example, it often happens in pharmaceutical industry that no more than one milligram of a sample of a new preparation is synthesized and thus available for all analysis techniques in the industry, which creates problems in its study by standard thermal analysis [1–5]. The ability to work with ultrasmall quantities of substances is also required in studies of the thermal behavior of high-energy materials, both in terms of safety and risks associated with the detonation process and due to the necessity of their detection in public places [6–8]. However, completely new technologies are required to apply analytical methods to such small quantities of samples, because conventional approaches in this case are not effective. For example, the improvement of methods of differential scanning calorimetry (DSC) to analyze ultrasmall quantities of substances has led to fundamental changes in implementation of this technique. Nanocalorimetry, or calorimetry on a chip is designed to work with samples of a few nanograms in weight, was proposed for the first time by Allen and colleagues in 1993 [9–11]. This group of scientists apparently for the first time conducted quantitative measurements using

samples such as ultrathin organic and inorganic films and individual polymer single crystals, which are inaccessible to conventional methods calorimetry [12–14]. An instrumental implementation of nanocalorimetry became possible because of the development of new MEMS nanocalorimetric sensors, in fabricated with the help of silicon technologies. The active area of the sensor is located on the surface of a silicon nitride membrane with low thermal conductivity, with the thickness of 1 μm ; this area is bounded by an electric circuit assembled on the membrane. The sensor is heated when passing electric current through the heating elements, while the temperature of the sample is measured with the help of six thermocouples disposed along the perimeter of the active area of the sensor and connected in series. Due to the low thermal inertia of the sensor, the heating and cooling rates of the sample are in the range of 10^3 – 10^6 $^\circ\text{C/s}$, making it possible to study samples having extremely small dimensions and weight. Despite the growing popularity of this method and a significant expansion of the application of thermal analysis of materials, a combination of calorimetry with other physical and chemical methods of analysis is even more promising, because solely calorimetric curves are often not enough to explain the mechanisms of complex transitions that occur during thermal treatment. An analysis of published data shows that successful attempts have been made on the combination of nanocalorimetry with mass spectrom-

etry [15], transmission electron microscopy [16], and X-ray diffraction [17–19]. In the latter case, a complex method was used to examine the phase behavior of various metal alloys; the implementation of the method involved ex situ experiments on the thermal and structural properties of materials. Furthermore, ex situ combination of nanocalorimetry with synchrotron X-ray diffraction was used to study the phase behavior of such materials as polyamide-6 and isotactic polypropylene [20]. However, to our knowledge, works devoted to the in situ combination of nanocalorimetry with the methods of nano- and microfocus synchrotron X-ray diffraction to study organic materials have not yet been published. This integrated approach would offer, for example, a solution of the problem of local study of the complex microstructure and thermodynamics of semicrystalline polymers.

A new and unique instrument called a nanocalorimeter having an open interface is described in previous works of our group; this device makes it easy to organize a combination of methods of thermophysical analysis with optical microscopy, both transmission and reflection [21, 22]. The main advantage of the device over the commercially available Flash DSC1 instrument from Mettler Toledo is that the measurement cell with a nanocalorimetric sensor is separated from the control-and-measuring unit. This fact offers the opportunity to perform nanocalorimetric research simultaneously with not only experiments on optical microscopy, but also X-ray diffraction, nanofocus synchrotron X-ray diffraction, mass spectrometry, atomic force microscopy, and others. The first successful experiments on combining nanocalorimetry with nanofocus synchrotron X-ray diffraction were set for the study of metal microparticles of various sizes [23–26]. In the present paper, we describe the first application of this complex method to study the structure formation processes in the semicrystalline samples of typical aromatic polyester, poly(trimethylene terephthalate), and to explain the mechanisms of polymer melting.

EXPERIMENTAL

We performed experiments on X-ray scattering using a nanosized beam in a ID13 nanofocus line of the European Synchrotron Radiation Facility (ESRF) (Grenoble, France). This line is unique, because it gives the researcher a wide range of possibilities for experiments on combining the diffraction of nano- and micro-dimensional X-rays with other physical and chemical methods of analysis. In these experiments, we used a nanosized beam focused to a size of approximately 100 nm using a Fresnel cross lens system, focusing the beam precisely to the required size with the least loss of its intensity. The energy of photons used in the experiments was 12 keV; diffracted photons were recorded using a FreLon CCD detector. This device was used to scan the samples and plot the

maps composed of two-dimensional high-resolution diffraction patterns. Samples were scanned using special precision motors for moving the sample holder. The experimental data were adjusted according to algorithms developed by the staff of the ID13 line. The adjusted experimental data were processed using a two-dimensional integration implemented in the IgorPro environment (Wavemetrics). In processing the data, we used the calibration data for diffraction peaks of silver behenate to calculate the scattering vector s ($|s| = 2\sin(\theta)/\lambda$).

To obtain nanocalorimetric data, we used a device created in our lab: a nanocalorimeter; it includes MEMS sensors manufactured by Xensor and enables in situ experiments on combining nanocalorimetry with other physical and chemical methods of research. This device offers the performance of high-precision AC and DC nanocalorimetric experiments using various preset temperature programs. The sensitivity of the system is 1 nJ/g with a high time resolution of 5 ms. The size of the active area of a XEN 39392 nanocalorimetric sensor used was $100 \times 100 \text{ mm}^2$. The nanocalorimeter controller is governed by the developed software supporting all versions of Windows, starting with Windows XP. The scheme of experimental setup is shown in Fig. 1.

The material used in this work is poly(trimethylene terephthalate) with a weight-average molecular weight of $M_w = 35200 \text{ g/mol}$ and a polydispersity of $M_w/M_n = 2$; it was received from Shell Chemicals (trademark Corterra CP 509200). Polymer pellets were melted at 230°C , and then fiber with a diameter of approximately $15 \mu\text{m}$ was obtained by melt extrusion. Further, $50\text{-}\mu\text{m}$ fragments of fiber, produced using a micro-scalpel, were applied to the center of the active area of the nanocalorimetric sensors using a micromanipulator. Prior to isothermal crystallization, samples were annealed at 230°C for 1 min in order to “erase” their structural memory. Next, the polymer samples were subjected to sharp cooling (more than 3000°C/s) and subsequent isothermal crystallization from the melt in a wide temperature range from 150 to 211.5°C . The image of a typical sample of poly(trimethylene terephthalate), crystallized at 180°C , is shown in the micrograph (Fig. 2).

In nanocalorimetric experiments, the sample weight can be calculated in two different ways: by calculating it from the geometric dimensions of fiber and the density of the material or based on the parameters of characteristic thermal transitions detected in the nanocalorimetric curves of heating and cooling of the sample. In this work we used both methods of calculation; the estimated weight for the given sample is $80 \pm 5 \text{ ng}$.

For in situ experiments on the study of the mechanisms of (trimethylene terephthalate) melting, nanogram samples were isothermally crystallized at 200°C

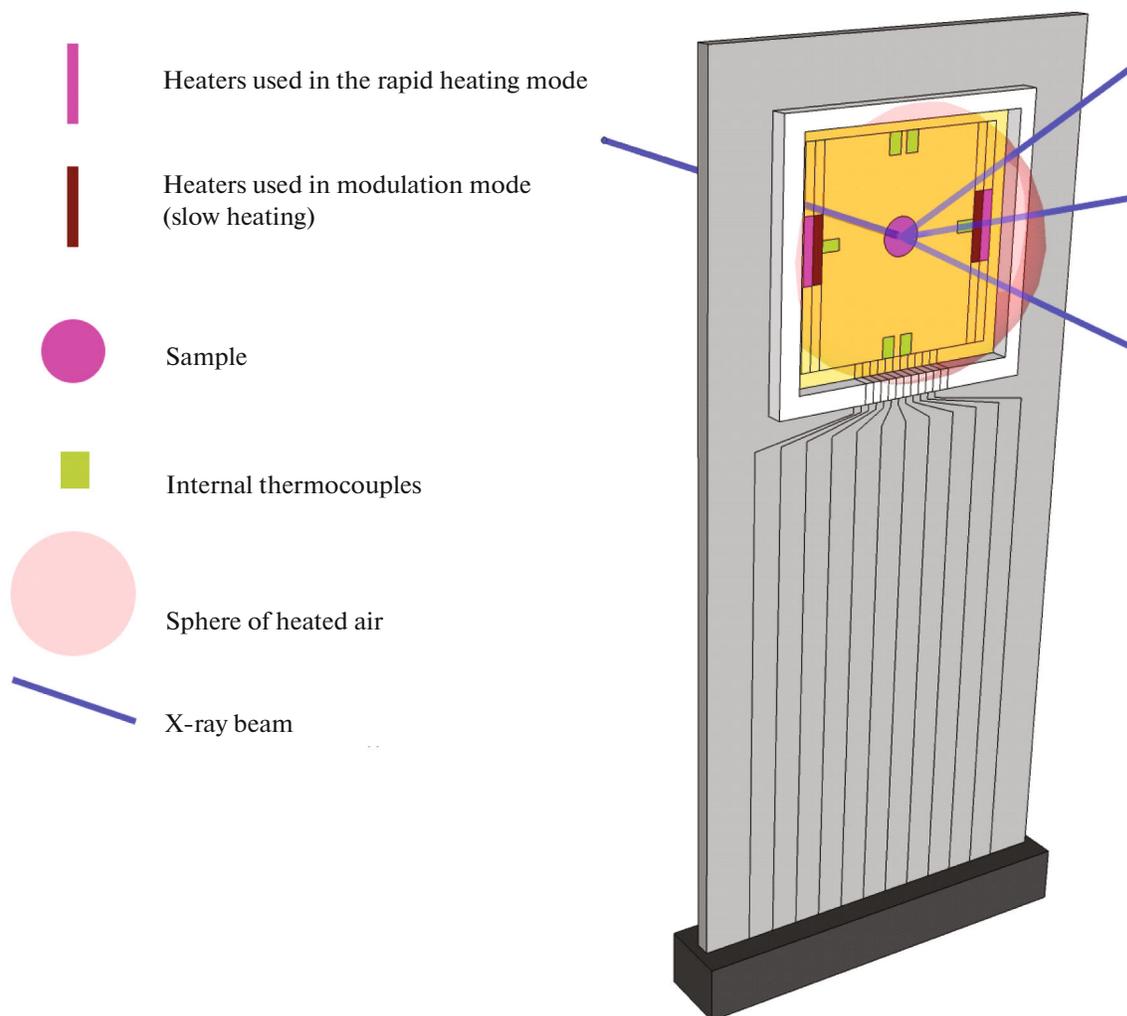


Fig. 1. Schematic representation of the installation on the combination of nanocalorimetry and nanofocus synchrotron X-ray diffraction. The direction of travel of X-rays and their subsequent scattering is indicated by blue lines. The gray parallelepiped corresponds to a nanocalorimetric sensor installed in the nanocalorimeter holder. The diagram presents the key components of the electrical circuit of the nanocalorimetric sensor: two pairs of heaters used in different modes and six internal thermocouples.

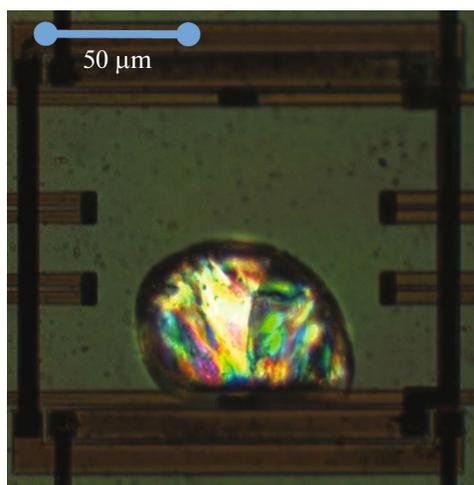


Fig. 2. Polarized light micrograph of the active area of a XEN 39392 nanocalorimetric sensor with a sample of poly(trimethylene terephthalate) crystallized at 180°C.

for 20 min and then briefly annealed at temperatures from 151 to 208°C using a heating and cooling rates of 1000°C/s. The crystallization process was monitored using a combination of nanocalorimetry with polarizing optical microscopy.

RESULTS AND DISCUSSION

The crystallization processes of poly (trimethylene terephthalate) from the melt were studied at each of the selected temperatures by observing the spherulite growth process through a polarization optical microscope. After completing the isothermal crystallization from the melt at temperatures from 150 to 211.5°C with increments from 2 to 4°C, the samples were used for nanocalorimetric measurements. The nanocalorimetric curves corresponding to some of the results are presented in Fig. 3.

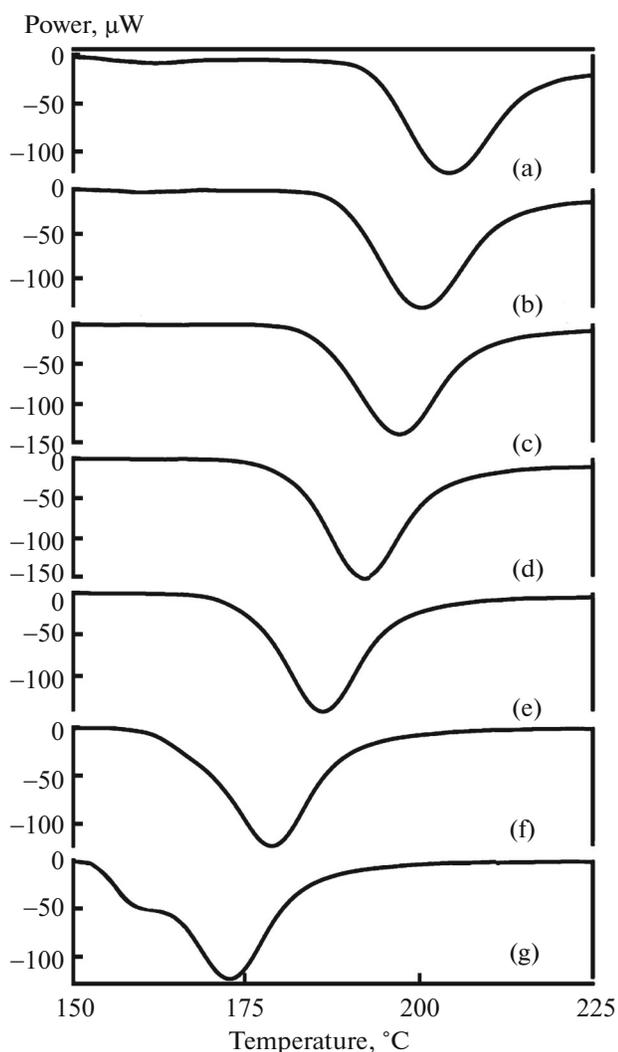


Fig. 3. Nanocalorimetric curves obtained during heating of poly(trimethylene terephthalate) crystallized from the melt at temperatures of (a) 211.5, (b) 204.3, (c) 200.3, (d) 193.0, (e) 179.7, (f) 170.0, and (g) 150.0°C; heating rate is 1000°C/s; test sample weight is 80 ± 5 ng.

As was shown in Fig. 3, the melting peak is shifted to higher temperatures with the increase of crystallization temperature, which corresponds to the formation of more thermodynamically stable crystals of poly(trimethylene terephthalate). The dependences of the initial melting point on the crystallization temperature are plotted in Fig. 4. A linear dependence is seen in the graph in the crystallization temperatures range from 150 to 196°C. This linear dependence corresponds to the conventional concepts of thermodynamics of crystallization of polymers and is used to determine the equilibrium, or thermodynamic, melting point of polymer [27]. In the described procedure of Hoffman–Weeks, this equilibrium melting point is found as a point of intersection of the dependence of the melting point of the polymer on the

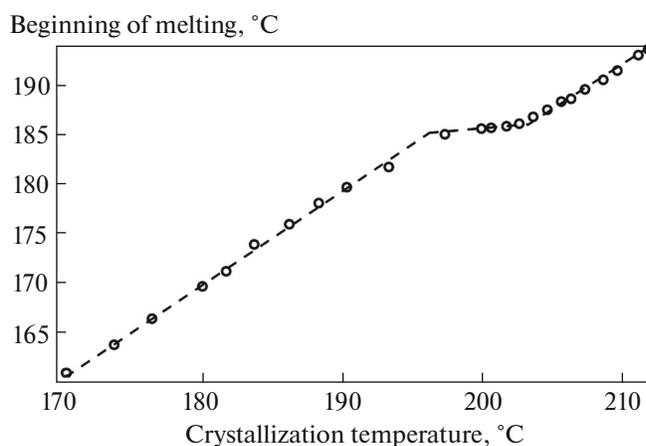


Fig. 4. Dependence of the onset of the melting peak on the crystallization temperature of poly(trimethylene terephthalate).

crystallization temperature, extrapolated linearly, with a straight line of $y = x$; that is, it is assumed that, at the equilibrium melting temperature, those crystals grow the melting point of what is the exact crystallization temperature.

However, the linear relationship is broken above this temperature range, and a break in the curve is seen at temperatures of approximately 196°C. The observed behavior calls into question the approach of linear extrapolation; this can be explained by the complex mechanisms of melting processes upon the heating of crystallized samples. Indeed, in the melting curve corresponding to the lowest crystallization temperature (150.0°C), a low-temperature melting peak is clearly seen, which reflects the well-known phenomenon of multiple melting of semicrystalline polymers with semirigid chains [28, 29]. With an increase in the crystallization temperature, this low-temperature peak becomes indistinguishable against the background of the main melting peak. We can assume that this two-stage nature of melting results in a deviation from the linear dependence of the melting point on the crystallization temperature of the melt because of the complex nature of the melting peak.

Previously, we have shown using small-angle X-ray scattering that the melting process of semicrystalline polymers with semirigid chains is a multistage process [30–34]. At the beginning of melting, the polymer crystals are melted that were formed during the secondary crystallization in the smallest amorphous regions of the semicrystalline structure. Despite the fact that these crystals are neither thinner nor more defective than the main population of crystals, their early melting can be explained by the effect of negative pressure formed in the condensing of material limited by the walls of small-sized amorphous cavity. Upon further heating, the partially molten polymer structure can undergo rapid reorganization, during which new

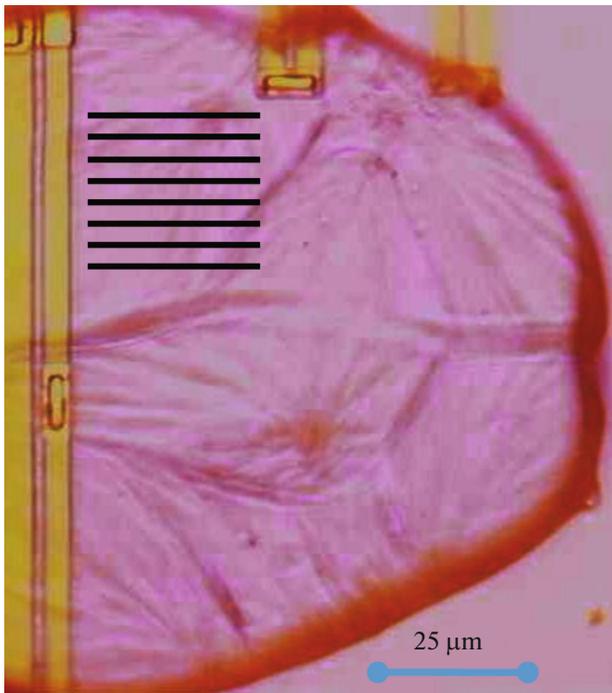


Fig. 5. Micrograph of the sample annealed for 5 ms at a temperature of 151°C after isothermal crystallization from the melt at 200°C. The black lines show the region of the linear scanning with an X-ray nano-focused beam.

tallization processes occur at rates much greater than the rate of crystallization of the polymer from the melt, which explains the difficulty of observing these processes using heating rates characteristic of conventional DSC. In our previous studies [30–34], we have not had the technical ability to trace the changes in the microstructure of the polymer during melting in real time.

In the present work, we used a unique combination of nanocalorimetry and synchrotron small-angle scattering for a better understanding of the processes occurring during crystallization and subsequent heating of samples of poly(trimethylene terephthalate). For example, to visualize the changes in the sample structure during heating, several experiments were made on the crystallization of the samples from the melt at a temperature of 200°C, further quenching of the samples to room temperature at 3000°C/s, and subsequent short annealing sessions at temperatures from 151 to 208°C. The annealing time at each temperature was 5 ms, and the heating and cooling rate was 1000°C/s. These quenching conditions completely exclude the possibility of restructuring of the samples during the actual linear heating and cooling, thus making it possible to fix the structure formed at different stages of melting. For this purpose, poly(trimethylene terephthalate) samples, having a spherulitic structure, were scanned with an X-ray nanofocus beam with a pitch of 1.5 μm after each heating, as is shown in Fig. 5 by the example of one annealing temperature.

crystals with improved thermodynamic parameters and an increased long period are formed in the molten regions [35]. It is important to note that such recryst-

The resulting two-dimensional diffraction patterns of small-angle X-ray scattering are presented in Fig. 6.

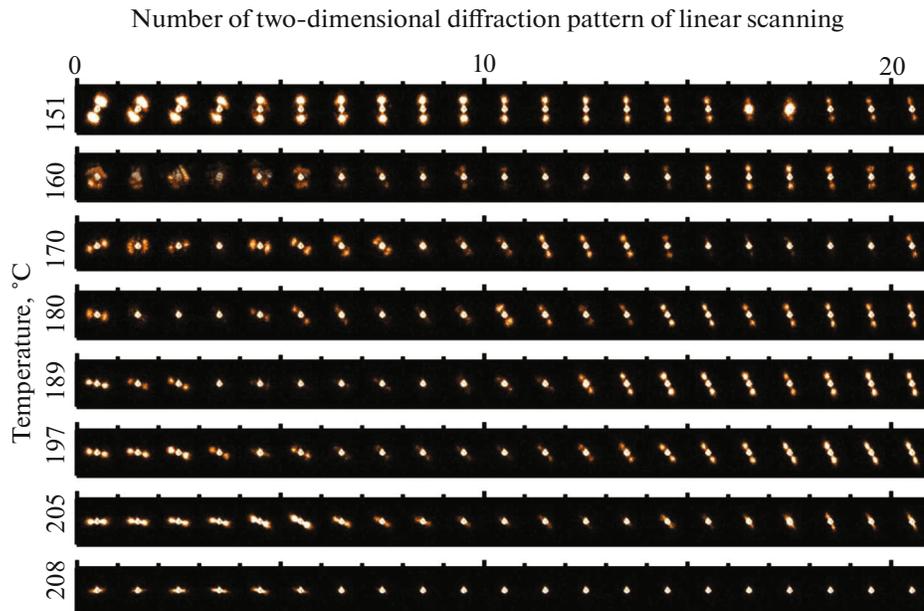


Fig. 6. Two-dimensional diffraction patterns of small-angle X-ray scattering (SAXS) obtained in the linear scanning of samples with a step of 1.5 μm. Diffraction patterns were recorded for the samples annealed for 5 ms at temperatures from 151 to 208°C immediately after their isothermal crystallization from the melt at 200°C. The heating rate of samples to reach the annealing temperature and the subsequent cooling to room temperature is 1000°C/s.

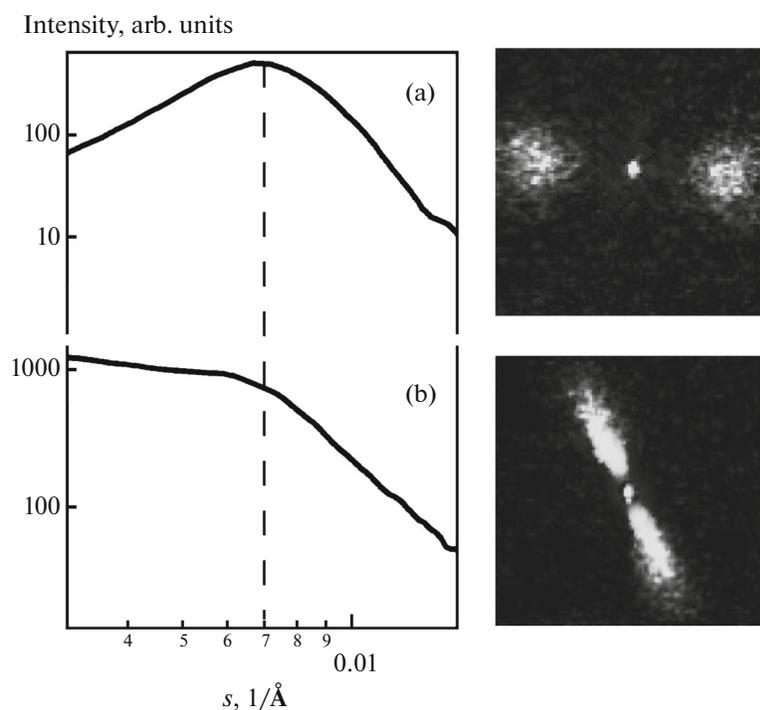


Fig. 7. One-dimensional SAXS profiles (left) obtained by integrating the corresponding two-dimensional diffraction patterns (right): (a) oriented SAXS profiles corresponding samples crystallized at 200°C and annealed at 151 and 160°C for 5 ms and (b) streaky SAXS profiles corresponding samples crystallized at 200°C and annealed at 205 and 208°C for 5 ms.

It is seen from the figure that, up to the annealing temperature of 197°C, two-dimensional small angle X-ray scattering (SAXS) images are well-oriented two-point diffraction patterns in which the main interference maximum corresponds to the average distance between two adjacent lamellar crystals. Good orientation of the diffraction patterns is explained by the local ordering of lamellar packs in spherulite on the scales that are significantly smaller than the diameter of a spherulite.

With a further increase of the annealing temperature to 205°C, a change in the small-angle X-ray scattering signal can be seen. In the first place, the distance between interference peaks begins to decrease, which corresponds to an increase in the distance between adjacent crystals. This change can be attributed to the start of melting of thermodynamically less stable crystals. Subsequently, the changes in the diffraction patterns become even more pronounced, and the two-point oriented diffraction patterns are transformed into so-called “streaks.” This type of SAXS signal indicates a violation of the long-range order in the packing of poly(trimethylene terephthalate) crystals forming lamellar packs, at which a clear interference maximum vanishes. By integrating the received two-dimensional diffraction patterns, we constructed one-dimensional profiles of small-angle X-ray scattering corresponding to the two fundamentally different types of two-dimensional diffraction

patterns. The obtained SAXS profiles are shown in Fig. 7.

It is seen in the figure that for the fully crystallized sample the main interference peak corresponds to $s = 0.07 \text{ \AA}^{-1}$ (the long period of 13 nm); it varies dramatically during short annealing at temperatures above 200°C, that is, above the temperature of isothermal crystallization from the melt. In case of SAXS profiles, the main interference peak does not appear for streaky diffraction patterns (Fig. 7b); the picture here corresponds to the scattering of individual crystals. It should be noted that, in the experiments with heating rates typical of conventional DSC, the formation of streaks does not occur because the system has time to recrystallize and form new lamellar packs with an increased long period. Thus, the use of the combination of ultrafast chip calorimetry and nanofocus synchrotron X-ray scattering described in this paper enables the quantitative study of the complex process of melting of semicrystalline polymers to create more accurate models of microstructural changes occurring during melting.

CONCLUSIONS

In the present work we developed and successfully applied a comprehensive experimental research method which consists of combining nanocalorimetry with nanofocus synchrotron X-ray diffraction to study

samples of the weight of a few nanograms. This method was used to study the processes of structure formation and melting of a typical aromatic polyester, poly(trimethylene terephthalate). Nanocalorimetric curves corresponding to the melting of the samples upon heating at 1000°C/s indicate the complex nature of the melting process of the polymer under study, but do not give complete information about the structural processes taking place during melting. The evolution of the structure of the sample crystallized at 200°C and subjected to short-term annealing at different temperatures was studied by small angle X-ray scattering. In particular, it was demonstrated that, upon heating above the crystallization temperature, well-oriented diffraction patterns consisting of two symmetrical areas of high intensity are transformed into streaky diffraction patterns, indicating a violation of a long order in the packaging of poly(trimethylene terephthalate) crystals.

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