Feature article

Insights into polymer crystallization and melting from fast scanning chip calorimetry

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ABSTRACT

Fast scanning chip calorimetry in its non-adiabatic version allows for heating and cooling at rates up to 10^6 K s^{-1}, covering all polymer processing relevant rates. Furthermore it allows for systematic studies of nucleation, crystallization, melting and reorganization for a large number of polymers. After an introduction, open problems and the need for further investigation of polymer crystallization are explained, followed by a brief description of the novel technique of fast scanning chip calorimetry and its capability to shed further light on fundamental details of the polymer-crystallization process. In the fourth part, specific examples of non-isothermal and isothermal crystallization studies are provided, including the discussion of the effect of nucleating agents. The possibility to investigate homogeneous nucleation and its kinetics is highlighted too. The fifth part focuses on the analysis of the melting kinetics and the determination of the zero-entropy-production melting temperature.

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1. Introduction

Crystallization and melting of macromolecules is different from low molecular mass molecules because of the chain structure [1–5]. Crystallization of the melt at high supercooling [1,6–8], and melting of crystals at high superheating [1,9–12] can be achieved by fast cooling and heating, respectively [13,14]. For most polymers it is possible to adjust crystal-free amorphous/glassy states and even formation or activation of nuclei may be suppressed at sufficient fast cooling. Studying these effects, that is, crystallization at high supercooling of the melt and melting of superheated crystals is on the one hand of interest for a better fundamental understanding of crystallization and melting of polymers, in particular in the shed of light of the underlying molecular processes. On the other hand, the polymer industry searches for materials with short processing times, and therefore fast crystallizing materials are preferable. Conventional experimental techniques applied for studying polymer crystallization and melting like differential scanning calorimetry (DSC) or X-ray scattering techniques do not allow studying the relevant processes with the needed time resolution, or cooling and heating rates, though significant progress is made regarding time resolution of X-ray scattering by using synchrotron radiation in combination with fast detectors [15–19], or, as the next step, by using ultra-short X-ray pulses [20,21]. However, fast and controlled (linear) cooling or heating is still not possible in such setups. On the other hand, in the last 10–20 years significant progress regarding high and controlled scanning rates up to 10^6 K s^{-1} was achieved in calorimetry. The pioneering work by Allen et al. [22–26] initiated several activities in the field of fast scanning chip calorimetry (FSC) on heating and cooling. Since that time, starting about 20 years ago, a significant number of papers dealing with polymer crystallization and melting under conditions of fast controlled temperature changes were published. This paper aims to highlight the power of the new technique for the study of polymer crystallization and melting.

On a few examples there will be discussed the benefits of fast scanning chip calorimetry. After discussing crystallization on cooling and at isothermal conditions, a route to generate samples free of homogeneously formed nuclei at temperatures above and below the glass transition temperature is presented. Since heterogeneities are never completely absent in a polymer melt, a strategy to minimize their impact on the observed crystallization is discussed. Making use of fast scanning chip calorimeters and combining both approaches, finally, allows studying the kinetics of formation of homogeneous nuclei under isothermal conditions.

Ultra-fast heating suppresses recrystallization and reorganization, and enables examination of melting events without the influences of those processes. In addition, variation of the heating rate permits quantitative analysis of the kinetics of such crystal-reorganization processes.

The paper is structured as follows. First a brief introduction to polymer crystallization/melting and FSC is provided. The next two main parts deal with the application of FSC to crystallization and melting. A summary and an outlook follow.

2. Polymer crystallization

The special character of polymer crystallization has been of interest for decades since a large number of polymers are

semicrystalline [27]. Nevertheless, a general understanding of polymer crystallization has not yet been achieved [28,29]. In recent years new concepts describing polymer crystallization were developed. In particular, ideas put forward by Strobl [2,30], Muthukumar [31], Olmsted, Ryan [32], Wunderlich [1,33,34] and others have challenged the Hoffman–Lauritzen theory [35]; for a detailed discussion see The European Physical Journal E Vol. 3, No. 2 (October 2000) pp 165–200. Nevertheless, the general concept of the classical nucleation theory suggesting first the formation of stable crystal nuclei which then is followed by their growth is still widely accepted.

Polymer crystallization usually takes place far from equilibrium with kinetically controlled mechanisms [30]. Typically, crystallization occurs between the glass transition and a temperature rarely higher than 5 K below the melting transition of slowly cooled samples. Molecular processes at such non-equilibrium conditions may only rigorously be followed by molecular-level simulations, such as molecular dynamics (MD) or Monte Carlo (MC) methods [36–39]. However, due to extremely slow dynamics and high complexity, polymer crystallization, so far, was impossible to model using conventional molecular simulations [31,37]. In a recent attempt, Luo and Sommer performed MD simulations for crystallization and melting of a polymer on cooling and heating at rates of about 2×10^7 K s^{-1} [40–45]. These scanning rates, now available in computer simulations, are close to the rate of 10^6 K s^{-1}, which experimentally is possible in FSC in both, heating [46] as well as cooling [47].

For a direct comparison of experimental and computer-simulation data another point has to be considered. In most computer simulations homogeneous nucleation is the starting point of crystallization, while in experiments crystallization may also be initiated by heterogeneous nuclei. FSC, however, is one of the few techniques allowing fast enough cooling to avoid heterogeneous nucleation on cooling of bulk samples [48–51], and to enforce homogeneous nucleation as earlier only observed at slow cooling in droplet experiments [52–55]. While in droplets with a size below a critical value the occurrence of one homogeneously formed nucleus is commonly sufficient to observe complete crystallization of the whole droplet, in bulk samples FSC is able to follow the development of homogeneous nuclei and their growth to crystals until impingement. It is therefore an attractive task to study crystallization and homogeneous nucleation processes at short time and, consequently, short length scales, approaching those of MD simulations. Even though at the moment the time scales do not overlap, there is a good chance to reach this goal in the near future due to progress in computation as well as calorimetry; details about the capacity of FSC analyses in order to approach conditions used in simulations are provided in the next chapter.

Making use of an self-made differential fast scanning chip calorimeter (DFSC) [56,57] and the commercial realization by Mettler Toledo, the Flash DSC 1 [58,59], we have studied isothermal nucleation and crystallization of fast crystallizing polymers, particularly poly(ε-caprolactone) (PCL), covering times from 10^{-4} to 10^5 s and temperatures from about 25 K below the glass transition temperature T_g (=209 K on cooling at 10 K/min [60]) up to 330 K, which is close to the equilibrium melting $T_{m,0}$ (=342 K [60]). With FSC we were able to follow the isothermal development of crystals over 9 orders of magnitude in time [51]. The final result of such an