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Book of Abstracts



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PLLA NUCLEI STABILITY IN DIFFERENT CONDITIONS ACCORDING TO CLASSICAL NUCLEATION THEORY

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By using fast scanning calorimetry (FSC) the influence of the transfer of poly(L-lactic acid) (PLLA) nuclei from the nucleation stage at low temperature (T_{nuc}) to the growth stage at higher temperature (T_d) as well as heating to the $T_{spike} > T_d$ on the stability of the nuclei was systematically studied. After experiments cluster size distribution during isothermal nucleation of PLLA at 60 °C for different nucleation times was estimated. It was found out that obtained calorimetric results are in qualitative agreement with the predictions of CNT.

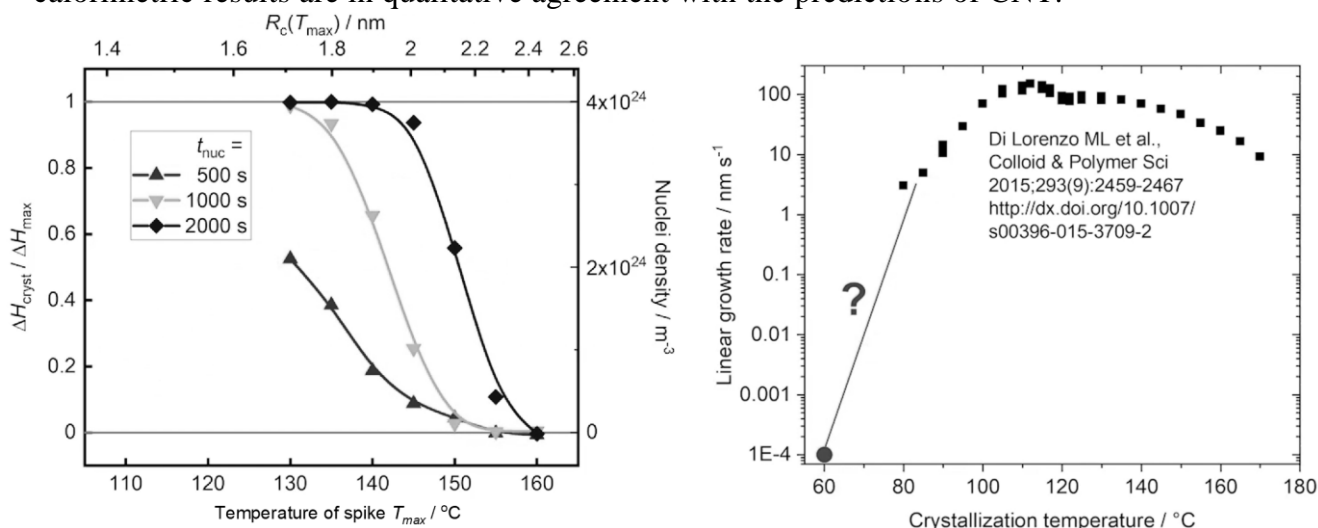


Fig. 1. Dependence of the enthalpy of melting of PLLA on the nucleation time at 60 °C and the spike temperature to which transfer heating is performed, preceding the stage of growth of nuclei to crystals (left). Growth rate of the clusters during nucleation (right).

The goal of the future research is to find out whether the data points for other low nucleation temperatures in right figure converge with the data already obtained by Di Lorenzo.

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ORIGIN OF ANNEALING PEAKS IN DSC/FSC HEATING SCANS OF SEMICRYSTALLINE POLYMERS

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The origin of endothermic annealing peaks in calorimeter heating scans of semicrystalline polymers is investigated in the shed of light of secondary crystallization and relaxation of a rigid amorphous fraction. Samples of poly (butylene succinate) (PBS) and poly (L-lactic acid) (PLLA) were crystallized at high temperature and subsequently rapidly cooled to the target annealing temperature. After the annealing step, the observed annealing peaks were evaluated regarding the enthalpy-change, while the evolution of the solid fraction was monitored by analysis of the heat capacity at a temperature higher than the glass transition temperature and lower than the annealing temperature. For both polymers it was found that the enthalpy-change scales with the increase of the solid fraction/crystallinity during annealing, thus suggesting that annealing peaks are caused by secondary crystallization but not relaxation of a rigid amorphous fraction.

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VAPORIZATION THERMODYNAMICS OF N-ALKYL BENZOATES: RECONCILIATION OF THE LITERATURE DATA, MEASUREMENT, AND PREDICTION

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The compounds of the homologous series of n-alkyl benzoates have a number of important applications. As for many low-volatile compounds, a few data on the vaporization thermodynamics of this class of compounds is available.

We systemized and critically analyzed all available information on vapor pressures and vaporization enthalpies of linear alkyl benzoates and complemented these data by additional experimental investigation of long-chained compounds. We used a recently developed experimental method for low vapor pressure determination¹ to measure vapor pressures and derived related thermodynamic functions of vaporization of pentadecyl, hexadecyl and heptadecyl benzoates.

Basing on experimental data and self-empirical approaches, we completely described the vaporization thermodynamics of a wide row of alkyl benzoates from methyl to eicosyl and established the correlation of some properties with the chain length. As a result, the following chain length dependences of vaporization enthalpy and natural logarithm of vapor pressure at 298.15 K were found:

$$\Delta_1^g H(298.15\text{ K}) / \text{kJ mol}^{-1} = 42.21 + 4.24 \cdot N_C, N_C > 1$$

$$\ln(P^\circ/\text{Pa}) (298.15\text{ K}) = 5.35 - 1.06 \cdot N_C, N_C > 1$$

A way for the prediction of vaporization enthalpies and vapor pressures inside the homologous series in the wide temperature range, based on previously found correlation for estimation of the heat capacity of vaporization^{2,3}, was proposed.

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DETERMINATION OF THE VAPOR PRESSURE BY MEANS OF FAST SCANNING CALORIMETRY IN STAGNANT AND MOVING GAS.

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Nowadays, one of the most important problems of a physical chemistry is a reliable determination of the vapors pressures in a wide temperature range. However, scientists have an issue with the low volatility of compounds of interest at temperatures below degradation temperature detected by conventional methods. To overcome these difficulties was suggested an application of the fast scanning calorimetry method for high-speed thermogravimetry. Due to nanogram-scale in the FSC approach is the significantly enlarged surface-to-volume ratio compared to conventional tensimetric methods. Therefore, in many cases, the tiny droplet evaporates so quickly that only minor chemical decomposition occurs.¹ The FSC approach is based on the following equation:

$$p_{\text{sat}} = \frac{dm}{dt} \cdot \frac{RT_{\text{vap}}}{A_{\text{vap}} M_A \beta_c} \quad (1)$$

where p_{sat} is the saturation vapor pressure of the sample at temperature T_{vap} in Pa; dm/dt is the mass-loss rate in $\text{g}\cdot\text{s}^{-1}$; A_{vap} is the vaporization/sublimation interface area in m^2 ; M_A is the molecular mass of the sample in $\text{g}\cdot\text{mol}^{-1}$; R is the universal gas constant, $8.314462 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and β_c is the mass-transfer coefficient in $\text{m}\cdot\text{s}^{-1}$.

Temperature, mass-loss rate, and evaporation surface area can be determined experimentally. To determine the mass-loss rate the sample is partially evaporated/sublimed during the high-temperature isotherm at T_{vap} and the mass of the sample was measured before and after the evaporation process. The evaporation surface area was calculated with Eq. (2) based on the assumption that the sample after premelting has the shape of a spherical cap

$$A_{\text{vap}} = \pi(a^2 + h^2) \quad (2),$$

where a is the base radius of the circular droplet and h is its height in the center.

The mass transfer coefficient requires special attention, and several assumptions are needed for its evaluation.

In our work was developed and experimentally verified procedure for determination of β_c in case of stagnant and moving surrounding gas B.

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KINETICS OF EQUILIBRIUM RECOVERY IN GLASS FORMING SYSTEMS BY FAST SCANNING CALORIMETRY

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The present contribution aims to unveil how advanced calorimetric techniques, including new generation fast scanning calorimetry, can highlight information of utmost importance on the kinetics of non-equilibrium in glassy materials. I will first give a glance on well-established facets of the transformation from a liquid into a glass, the so-called vitrification or glass transition, and the evolution of the glass thermodynamic state, generally addressed as physical aging. Subsequently, I will show how recent activity on a variety of glasses revealed the presence of different molecular/atomic mechanisms triggering both vitrification and physical aging, thus questioning the common view exclusively emphasizing the role of the primary (α) relaxation [1-2]. The presence of fast mechanisms of equilibration is emphasized in the light of their mild activation energy, which implies smooth increase of the equilibration time with decreasing temperature. This offers great potential to decrease the glass energy in time scales amenable to the experimental practice. In glasses exhibiting large amount of free interface, where equilibration is accelerated with respect to bulk glasses [3], energies down to the ideal glass, theorized long ago [4], can be achieved in time scales shorter than several days [5-6]. In the last part of the talk, the emphasis will be moved to the high temperature regime, specifically on the possible role of glass equilibration of non- α relaxation mechanisms. It will be shown on a preliminary basis that such mechanisms are active even above the amorphous material glass transition temperature (T_g) and become slower than the α relaxation. As a result, they give rise to aging above T_g , a completely new aspect of glass dynamics deserving further attention in the future.

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FAST SCANNING CALORIMETRY OF SILK

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Silk is a naturally occurring biopolymer which has been used in textiles for over 5000 years. The properties of silk protein are related to the secondary structures, such as helices, random coils and beta pleated sheet crystals. We have prepared the silk protein, fibroin, by extracting it from the native cocoons and use this as a starting material for our investigations. In this presentation, I will describe our studies to quantify the thermal and structural properties of silk using fast scanning calorimetry (FSC) measurements supported by X-ray diffraction and infrared spectroscopy. Silk degrades before melting when heated at conventional rates. We therefore used fast scanning chip-based calorimetry to heat and cool silk at 2000 K/s, the first time any fibrous protein had been studied in this manner.¹ Using FSC to minimize thermal degradation, we successfully demonstrated the melting behavior of beta pleated sheets¹, determined the liquid state heat capacity of silk fibroin², and provided a methodology for obtaining quantitative heat capacity in materials which can withstand only a single heating to high temperature³. We made preliminary estimates of the heat of fusion of beta sheets⁴ and studied the melting of two types of silk crystals⁵, Silk I and Silk II, showing that Silk II is the more thermally stable crystal form of silk.

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HIGH-TEMPERATURE BEHAVIOUR OF SOLID NATURAL CYCLODEXTRINS

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Natural cyclodextrins (CDs) are a class of cyclic oligosaccharides having molecular cavities. CDs are widely used in pharmaceuticals, cosmetics, food and textile industry, catalysis, chromatography. Undoubtedly, such important substances as cyclodextrins require accurate knowledge of fundamental thermodynamic properties: melting points and corresponding enthalpies. Such data are essential for understanding and predicting of properties based on structure-property relationships; for calculations on the energy of the crystal lattice, which has a crucial effect on inclusion properties; for evaluation of the limiting temperatures during the modification of drug complexes by fast heating and cooling. At the same time, the melting points and corresponding enthalpies cannot be measured by conventional methods, since solid CDs decompose without melting at temperatures less than 300 °C.

The present study is focused on the determination of the melting parameters and high-temperature behavior of natural cyclodextrins using fast scanning calorimetry (FSC). Melting points of α -, β - and γ -cyclodextrin were determined for the first time using FSC with heating rates up to 40000 $\text{K}\cdot\text{s}^{-1}$, also as melting enthalpy of γ -cyclodextrin. The activation energies of thermal decomposition of cyclodextrins were calculated from the temperature dependence at wide range of heating rates.

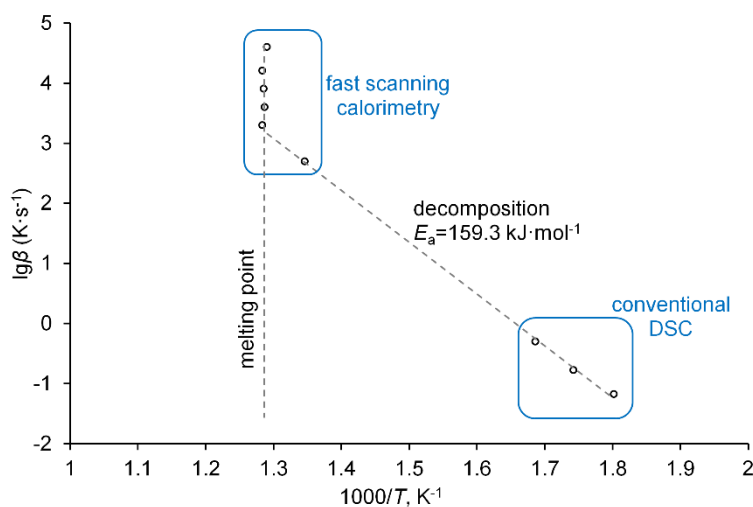


Figure 1. Dependency of onset temperatures (T) of main exothermic peak for anhydrous α -cyclodextrin on heating rate (β) in Flynn–Wall–Ozawa analysis coordinates.

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MELTING PROPERTIES AND SOLUBILITY OF AMINO ACIDS AND PEPTIDES

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Amino acids and peptides are most important substance classes in the chemical industry and biotechnology. The final products are often synthesized by fermentation and purified in a complex downstream process, for which the knowledge about the solubility of every single solute is mandatory. Since the determination of experimental temperature-dependent solubility data is time-consuming and cost-intensive, modeling solubility using physical properties such as melting properties is highly desired. Unfortunately, the direct determination of melting properties for amino acids and peptides using conventional DSC is not possible due to the decomposition before their melting at low heating rates. This was overcome by applying Fast Scanning Calorimetry (FSC) with heating rates up to 20,000 K s⁻¹ to measure the melting properties of 20 proteinogenic amino acids and 22 peptides with a focus on isomeric dipeptides and tripeptides.

The experimental FSC-measured melting properties were used as input data in the thermodynamic modeling framework PC-SAFT to model the solubility in water and in water+2-propanol solutions. Furthermore, three gE models (Wilson, NRTL, UNIQUAC) were applied to model solubility. The experimental determination of solubility in water and in water+2-propanol solutions was performed using the photometric method and the gravimetric method of supersaturated solutions. Additionally, the pH-value and the crystal structure were investigated to ensure the neutral species in solution and to exclude crystal structure changes in the solid phase. The PC-SAFT modeled solubility was finally compared to the experimentally determined solubility. Here PC-SAFT shows dramatically improved modeling accuracy compared to the gE models while using less binary parameters. The synergy between FSC and PC-SAFT opens the door for solubility modeling of biomolecules that decompose before their melting.

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CRYSTALLIZATION KINETICS OF THE ACTIVE PHARMACEUTIC INGREDIENTS FROM FAST SCANNING CALORIMETRY DATA

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Most of the currently applied active pharmaceutical ingredients are poorly soluble in water. One of the examples of such drugs are dopamine hydrochloride (DOP) and atenolol (ATE). There are different approaches for improving drug solubility. One of them is the preparation of the drugs in an amorphous form.

The biggest problem in dealing with the amorphous forms of the drugs is low kinetic and thermodynamic stability. There are several approaches to studying the crystallization tendency of the amorphous dosage forms including isothermal and non-isothermal methods. The isothermal method involves maintaining the temperature of the supercooled melt of the drug at storage temperature and determining the amount of the crystalline phase at certain intervals. Non-isothermal kinetics methods can be used to reduce the experiment time needed for determining the parameters of the kinetic equation, including activation energy (E_a), preexponential factor (A), and reaction model (g).

A promising approach for studying the stability of the amorphous form of the drugs is the evaluation of their glass-forming ability (GFA). The molecular mobility, glass-forming ability, and the stability of the glass are linked. Molecular mobility can be determined using the FSC technique. The first step of the evaluation is determining the activation energy of the vitrification. The kinetic fragility (m) can be calculated based on these data, providing a measure of the deviation of the temperature dependence of the viscosity or relaxation time from the Arrhenius-type dependence.

In the present work, the key parameters for the formation and stability of the glassy amorphous forms of the two rapidly crystallizing drugs dopamine hydrochloride and atenolol were determined using Fast Scanning Calorimetry.

The critical cooling rates of the melts of these active pharmaceutical ingredients were found to be $4000 \text{ K}\cdot\text{s}^{-1}$ (DOP) and $3000 \text{ K}\cdot\text{s}^{-1}$ (ATE). The kinetic fragility values of the produced glassy drugs were 43 (DOP) and 54 (ATE). According to a classification from the literature, the former is considered “strong“, and the latter is “moderately strong”. Atenolol having higher kinetic fragility must have the higher glass forming ability.

The kinetic stability of the produced glasses was investigated using both non-isothermal and isothermal approaches. The best agreement between the results of the two approaches is observed in the case of the Nakamura crystallization model.

The methodology for the assessment of the stability of the amorphous forms of drugs, described in the present work, can find application in the pharmaceutical industry for determination of the optimal conditions for preparation and storage.

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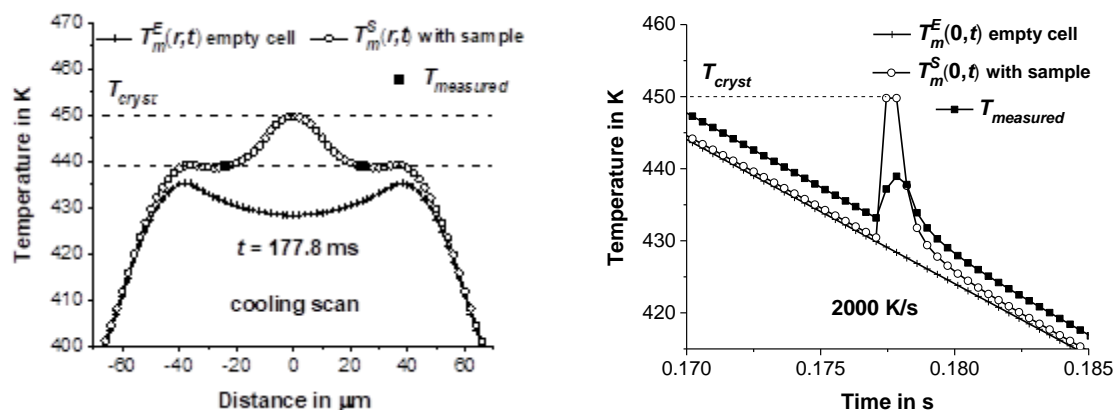
INFLUENCE OF TEMPERATURE GRADIENTS AND THERMAL CONTACT CONDUCTANCE ON MEASUREMENTS WITH ULTRAFAST CHIP CALORIMETRY

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When measuring with membrane (chip) calorimetry, temperature gradients and thermal contact resistance should be considered. The sample strongly influences the temperature gradients in the membrane, especially when the sample melts and crystallizes. We present the temperature distribution in the membrane $T_m(x,y,t)$ calculated for a commercial calorimetric chip (XEN-39391) loaded with a very small (1 ng) polymer sample. The effect of a melting (crystallizing) polymer sample on $T_m(x,y,t)$ and the temperature $T_{measured}$, measured at a distance from the center of the membrane, is calculated using method ¹ for a sample located at the center, see Figure below.



Similar calculations are presented for a 1.6 ng indium sample (sample parameters are the same as in Ref. ²). It is shown that the interfacial thermal resistance at the membrane/sample interface significantly affects the measurement of the sample temperature. The influence of temperature gradients and thermal contact resistance on the calorimetric measurements can be minimized if the temperature is measured exactly in the center of the hot zone of the calorimetric sensor, and the thermal contact conductance of the thermal contact at the membrane/sample interface is high enough.

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STUDYING REVERSIBLE PROTEIN DENATURATION BY THE STEP SCAN CALORIMETRY, RESULTS OF MODELING AND EXPERIMENTS

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Despite the recent developments of the step-scan calorimetric technique in the field of polymer melting/recrystallization, glass transition, and physical ageing, the technique remains largely unused in the field of protein stability.

We have performed numerical modeling of the step-scan calorimetric curves of the protein denaturation in the two-state approximation. The quasi-equilibrium denaturation regime can be realized if the duration of isothermal steps is long enough so that the system is able to settle to equilibrium. The changes in the real and imaginary parts of the complex heat capacity during the denaturation process depend on the rate constant of denaturation. A simple procedure for thermal losses correction and adjusting temperature is discussed.

The practical application of the step scan method for denaturation of lysozyme in water has revealed the negative temperature coefficient of the excess heat capacity of the lysozyme. In the case of denaturation of lysozyme in glycerol studied by fast scanning calorimetry, the step scan technique can be used to improve the quality of the baseline and reveal a heat capacity step after denaturation.

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APPLYING ISOCONVERSIONAL KINETIC ANALYSIS TO FAST SCANNING CALORIMETRIC DATA: HOW AND WHY?

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Kinetic methods used in thermal analysis and more specifically to polymer crystallization can be applied to Fast Scanning Calorimetric data. The relevance of some of these methods will be briefly discussed and physically sounded methods will be presented.

Applications of these methods to FSC data makes it possible to greatly extend the temperature range and to have access to the characteristic parameters of nucleation and diffusion, which cannot be estimated with regular DSC for processes whose crystallization is very fast. Important information on fast crystallization processes, changes on crystallization mechanisms and prediction of temperature at maximum growth rate can be obtained by analyzing the apparent activation energy variations with temperature.

Examples of PTFE, PTFE nanocomposites with nanosilica clusters, PBS and PBS nanocomposites with graphene nanosheets will be discussed.

RELAXATION AND STRUCTURE FORMATION IN THE VICINITY OF THE GLASS TRANSITION

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In the vicinity of the glass transition amorphous materials are far of thermodynamic equilibrium and kinetically constrained. As a result, diffusion processes largely control structure formation. Structure formation in the glass transition region is discussed using the example of two different systems, an atomic compound (the bulk metal glass (BMG) forming alloy $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$) and a random copolymer (hydrogenated nitrile-butadiene rubber, HNBR).

The BMG forming alloy is prepared to form a chemically homogeneous glass (CHG) without quenched nuclei. During annealing below the glass transition, this material exhibits a sequence of the following steps: structural relaxation, incubation period, nucleation, crystallization and crystal perfection. The crystalline modification formed is different from the least stable modification formed above the glass process.

Crystallization in the copolymer is chemically confined. This material shows no kinetic distinction between relaxation and crystallization in the glass transition region. The results indicate that nanocrystals are initially formed by cooperative rearrangements and further growth is interrupted by the large amount of rigid amorphous fraction (RAF) simultaneously formed.

DETERMINATION OF THE (EQUILIBRIUM) MELTING RANGE OF POLYMER LAMELLAE

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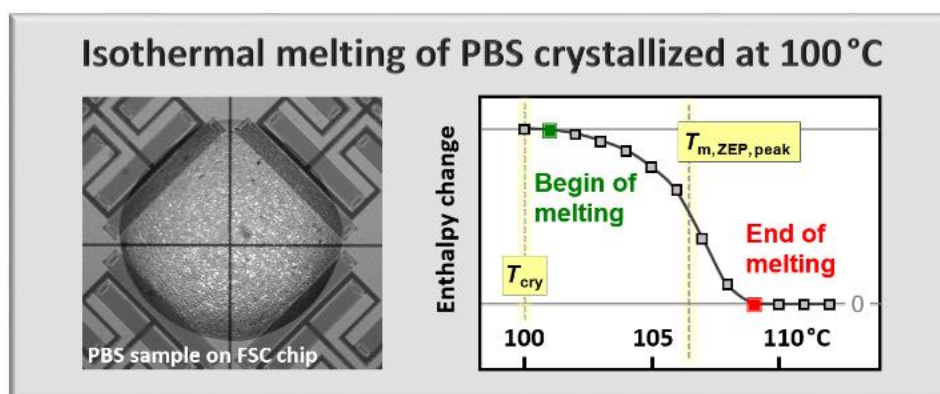
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Crystallization of poly(butylene succinate) (PBS) at 100 °C, about 30 K below the equilibrium melting temperature, allowed preparation of crystals which were analyzed regarding their zero-entropy production melting temperature.¹ Irreversible melting occurs in a rather narrow temperature window of only around 9 K, between 100 and 109 °C, revealing a narrow distribution of the thickness of isothermally formed lamellae and a rather low thickening/stabilization-factor of less than 1.4.



Quasi-isothermal temperature-modulated differential scanning calorimetry suggests significant reversible melting and crystallization during and after crystallization, proving existence of a large fraction of crystalline phase being at the stability limit at the crystallization temperature. Heating of crystals formed at 100 °C to above their zero-entropy production melting temperature, followed by isothermal annealing, permitted analysis of the kinetics of irreversible melting, yielding superheating-dependent rate constants of the order of magnitude of 10^2 s^{-1} 5-10 K above the zero-entropy production melting temperature. The advanced analysis of the melting behavior of isothermally at low melt-supercooling grown polymer crystals allows drawing conclusions about their (inherently) low thermodynamic stability

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AN APPROACH FOR THE CALCULATION OF THE VAPORIZATION ENTHALPIES OF ORGANIC NON-ELECTROLYTES AT AN ARBITRARY TEMPERATURE AND VERIFICATION OF THE APPROACH BY FAST SCANNING CALORIMETRY

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Vaporization enthalpy is one of the most important parameters for the description of vapor-liquid equilibrium in pure substances and mixtures. However, the experimental data on the vaporization enthalpy in the wide temperature range are rarely available.

In our laboratory a system of methods for the calculation of the vaporization enthalpies of organic non-electrolytes at 298.15 K was developed, based on solution calorimetry¹². For determination of the vaporization enthalpy in the wide temperature range one needs also to evaluate the difference between liquid and ideal gas phase heat capacities ($\Delta_{\text{g,p,m}}^1 c_p$).

In works³⁴ we shown that the latter difference can be found from a linear correlation with the vaporization enthalpy ($\Delta_1^{\text{g}}H$) at 298.15 K. Different correlations were established for aromatic and aliphatic compounds (SD < 4 J·K⁻¹·mol⁻¹):

$$\Delta_{\text{g,p,m}}^1 c_p (298.15 \text{ K})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 0.49 \cdot \Delta_1^{\text{g}}H (298.15 \text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) + 37.0 \quad (1)$$

$$\Delta_{\text{g,p,m}}^1 c_p (298.15 \text{ K})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 1.52 \cdot \Delta_1^{\text{g}}H (298.15 \text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) + 0.9 \quad (2)$$

The equations were derived based on the assumption that the difference between the liquid and gas phase heat capacity is primarily related to intermolecular interactions in the liquid. For alkylaromatic compounds, the combined equation was shown to be applicable.

Thus, after calculating $\Delta_1^{\text{g}}H$ (298.15 K), one can derive the vaporization enthalpy as a function of temperature according to Kirchhoff's law of Thermochemistry. Such approach was tested by calculating more than 1547 vaporization enthalpies of 731 aromatic, aliphatic compounds, and alkylarenes in the temperature range between 220 and 650 K. The calculated magnitudes were compared with the available literature data, the vaporization enthalpies of low-volatile aromatics determined by fast scanning calorimetry, and the values derived by widely used Chickos *et al.* scheme. In most cases, an agreement with the experimental data was within the limits of experimental error (RMS = 1.5 kJ·mol⁻¹). The performance of Chickos *et al.* scheme was comparable when the temperature range of adjustment was less than 100 K, but decreased in the wider adjustment intervals and for the larger molecules.

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CRYSTAL NUCLEATION IN POLYAMIDES

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Nucleation and crystallization of polyamide 12 have been systematically investigated by fast scanning calorimetry (FSC). Comparing the crystallization behavior of PA 12 with other polyamides, the activation energy for crystallization increases and the energy barrier of short-range diffusion decreases with the increase of the amide-group density in the chains. In addition, homogeneous crystal nucleation in polyamide 66 (PA 66) was studied by a combination of atomic-force microscopy (AFM) and fast-scanning-chip calorimetry (FSC), with a specific experimental setup allowing precise correlation of AFM images and FSC heating curves.

With the number of crystals/nuclei detected by AFM imaging, and by variation of the nucleation time, a steady-state nucleation rate of $(2.3 \pm 0.2) \times 10^{18} \text{ m}^{-3} \text{ s}^{-1}$ ($2.3 \mu\text{m}^{-3} \text{ s}^{-1}$) at 310 K has been determined. Comparing the total enthalpy of melting of the crystals, obtained by FSC, with the number of crystals, observed by AFM, yields the specific enthalpy of melting/formation of one single crystal at the specific growth conditions applied. Application of this approach, that is, correlating transition enthalpies with nuclei numbers, for analysis of crystal nucleation in a wide range of temperatures.

ALUMINUM ALLOYS SOLIDIFICATION DURING ADDITIVE MANUFACTURING, STUDIED BY FAST SCANNING CALORIMETRY

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Recent advantages of Fast Scanning Calorimetry (FSC) were found their application in additive manufacturing (AM). Particularly the size of the sample – 10-20 microns – as well as temperature scanning rate range – up to 100,000 K/s – fits perfectly to the process of laser rapid melting and solidification after it.

Cold cracking is a serious issue in AM. Extensive modification of traditional materials is required in order to match the conventional production mechanical properties. Can the FSC help to prove the modification efficiency using only a few AM powder particles, and thus reduce the cost of powder production?

A correlation between AM product microstructure and undercooling in FSC is discussed. Issues in temperature measurement at different rates are discussed and the solutions to overcome them is provided. The results include undercooling investigation of 6 variants of aluminum alloys AA7075 and on of AlN6.1, as well as few polymer composites.