For large amounts of text, e.g. in magazines, MTD Magazin is used. To ensure good readability, it is set in 11 pt type, and line spacing is 14 pt.

General rule: MTD Magazin is always justified. Avant Garde Condensed is always left-aligned and unjustified.
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Cooling rate dependence of the crystallinity at nonisothermal crystallization of polymers: a phenomenological model

Jürgen E.K. Schawe

Abstract
The cooling rate dependence of the crystallinity of polymers is investigated via the example of different technical polypropylenes using fast scanning calorimetry (FSC) in a cooling rate range between 1 and 5000 K s\(^{-1}\). In the slower cooling rate range (below 100 K s\(^{-1}\)) the crystallinity increases slightly with decreasing cooling rate. Above cooling at 100 K s\(^{-1}\) the crystallinity decreases substantially and vanishes at the critical cooling rate. We describe this behavior using a simplified model with two components: the generic crystallinity function and the retardation function. For a mathematical description, we use empirically fitted functions that describe the cooling rate dependence of the crystallinity and the critical cooling rate.

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Phase transitions and nucleation mechanisms in metals studied by nanocalorimetry: A review

Bingge Zhao, Linfang Li, Fenggui Lu, Qijie Zhai, Bin Yang, Christoph Schick, Yulai Gao

Abstract
Nanocalorimetry is profound in studying phase transitions in metallic materials for its ultrafast scanning rates and ultrahigh sensitivity compared with conventional calorimetric methods. This review illustrates recent findings in phase transitions and nucleation in metals employing nanocalorimetry. The melting behavior of nanoparticles was summarized. Furthermore, the glass transition, crystallization and martensite–austenite transformation were reviewed. Attributing to the ultrahigh sensitivity, small thermal changes in the solid reaction of the thin films were possible to be captured, which helped to understand its transformation mechanism. In rapid cooling processes, the nucleation of thin films and single droplets was conducted under controllable conditions, and the undercooling evolution was quantitatively investigated with different nucleation models. Moreover, the internal structures of samples after nanocalorimetric measurements were characterized using different methods. In summary, nanocalorimetry opens up a new field to reveal phase transitions in metallic samples, making it possible to compare the theoretical estimates and experimental results.
**Nanocalorimetry measurements of metastable states**

*John H. Perepezko, Trent W. Glendenning, Jun-Qiang Wang*

**Abstract**
Nanocalorimetry offers new capabilities to explore previously inaccessible domains of reaction kinetics due to the expanded heating and cooling rates compared to conventional calorimetry methods. With this capability it is now possible to explore ranges of alloy metastability and to examine rapid kinetic reactions such as melting and the competition between crystallization and glass formation. These capabilities are demonstrated for the melting of phases in Pb–Bi alloys, the melting and undercooling of Sn and glass formation in an organic compound D-mannitol.

**Nucleation behavior of melted Bi films at cooling rates from 10¹ to 10⁴ K/s studied by combining scanning AC and DC nano-calorimetry techniques**

*Kechao Xiao, Joost J. Vlassak*

**Abstract**
We study the nucleation behavior of undercooled liquid Bi at cooling rates ranging from 10¹ to 10⁴ K/s using a combination of scanning DC and AC nano-calorimetry techniques. Upon initial melting, the Bi thin-film sample breaks up into silicon nitride-coated isolated islands. The number of islands in a typical sample is sufficiently large that highly repeatable nucleation behavior is observed, despite the stochastic nature of the nucleation process. We establish a data reduction technique to evaluate the nucleation rate from DC and AC calorimetry results. The results show that the driving force for the nucleation of melted Bi is well described by classical nucleation theory over a wide range of cooling rates. The proposed technique provides a unique and efficient way to examine nucleation kinetics with cooling rates over several orders of magnitude. The technique is quite general and can be used to evaluate reaction kinetics in other materials.
Experimental determination of the nucleation rates of undercooled micron-sized liquid droplets based on fast chip calorimetry

Christian Simon, Martin Peterlechner, Gerhard Wilde

Abstract
Accurate thermal analyzes and calorimetry measurements depend on careful calibration measurements. For conventional differential scanning calorimeters (DSC) the calibration procedure is well known. The melting point of different pure metals is measured and compared with literature data to adjust the temperature reading of the calorimeter. Likewise, the measured melting enthalpies of standard reference substances serve for enthalpy calibration. Yet for fast chip calorimetry, new procedures need to be established. For the medium-area and large-area calorimeter chips, this procedure needs to be modified, because the calibration behavior depends on the position of the sample on the measurement area. Additionally, a way to calibrate the calorimeter for measurements performed during cooling will also be shown. For this second aspect, the athermal and diffusionless martensitic phase transformation of Ni49.9–Ti50.1 at% was used. The well-calibrated sensor chips are ideally suited to perform nucleation rate density analyzes based on a statistical approach. Here, the nucleation rate densities of micron-sized pure Sn droplets that had been coated with a non-catalytic coating have been determined by experimental analysis of the statistical variance of the undercooling response.

Reprint of: Characterization of bulk metallic glasses via fast differential scanning calorimetry

S. Pogatscher, D. Leutenegger, A. Hagmann, P.J. Uggowitzer, J.F. Löffler

Abstract
This study explores the thermophysical properties of Au-based bulk metallic glasses (BMGs) via fast differential scanning calorimetry (FDSC). Using this technique, the glass formation of the alloys Au60–xCu15.5–xAg7.5Si17 (x = 0.5 and 10) was investigated in situ. The critical cooling rate (F_c) and heating rate (F_h) required to avoid crystallization were analyzed for various sample masses and chip sensor surface materials. The results show that the alloy with the highest Au-content exhibits the lowest resistance against crystallization. Silicon nitride, silicon oxide and graphite used as chip sensor surface material were proven not to influence the measurements. In general, a dependence of crystallization on sample mass was observed for all compositions. Both the critical cooling and critical heating rates increase until a certain mass is reached. This phenomenon is explained via a size-dependent nucleation effect.
**Application of in-situ nano-scanning calorimetry and X-ray diffraction to characterize Ni-Ti-Hf high-temperature shape memory alloys**

*Patrick J. McCluskey, Kechao Xiao, John M. Gregoire, Darren Dale, Joost J. Vlassak*

**Abstract**

Combinatorial nanocalorimetry and synchrotron X-ray diffraction were combined to study the martensite–austenite (M–A) phase transformation behavior of Ni–Ti–Hf shape memory alloys. A thin-film library of Ni–Ti–Hf samples with a range of compositions was deposited on a parallel nano-scanning calorimeter device using sputter deposition. Crystallization of each amorphous as-deposited sample by local heating at approximately $10^4 \text{K/s}$ produced a nanoscale grain structure of austenite and martensite. Individual samples were then cycled through the M–A transformation, while the transformation enthalpy was measured by nanocalorimetry and the low- and high-temperature phase compositions were determined by X-ray diffraction. The techniques enable correlation of the observed behavior during thermal cycling with the thermodynamic and structural properties of the samples.

**Kissinger method applied to the crystallization of glass-forming liquids: Regimes revealed by ultra-fast-heating calorimetry**

*J. Orava, A.L. Greer*

**Abstract**

Numerical simulation of DSC traces is used to study the validity and limitations of the Kissinger method for determining the temperature dependence of the crystal-growth rate on continuous heating of glasses from the glass transition to the melting temperature. A particular interest is to use the wide range of heating rates accessible with ultra-fast DSC to study systems such as the chalcogenide $\text{Ge}_2\text{Sb}_2\text{Te}_5$ for which fast crystallization is of practical interest in phase-change memory. Kissinger plots are found to show three regimes: (i) at low heating rates the plot is straight, (ii) at medium heating rates the plot is curved as expected from the liquid fragility, and (iii) at the highest heating rates the crystallization rate is thermodynamically limited, and the plot has curvature of the opposite sign. The relative importance of these regimes is identified for different glass-forming systems, considered in terms of the liquid fragility and the reduced glass-transition temperature. The extraction of quantitative information on fundamental crystallization kinetics from Kissinger plots is discussed.
| 9 | **Thermochimica Acta 603 (2015), 69-78**  
**Nanocalorimetry study of the evolution of melting characteristics of single layer silver alkanethiolate lamella: Fast heating/cooling and electrical annealing**  
Zichao Ye, Lito P. de la Rama, Liang Hua, Mikhail Y. Efremov, Leslie H. Allen  
**Abstract**  
Nanocalorimetry (NanoDSC) is applied to measure the melting characteristics of single layer silver pentadecanethiolate (AgSC15) crystals. Its attribute of high sensitivity enables the characterization of single layer species. The fast heating (~50,000 K/s) and cooling (~10⁴ K/s) rates employed allow an *in situ* study of lamella layer evolution. By controlling the maximum temperature (T_{max}) achieved during heating/cooling cycles, the samples can be either melted or annealed. If T_{max} is larger than sample melting point (T_m), the first NanoDSC pulse shows the melting behavior of the as-synthesized crystal. The following rapid cooling (quenching) causes crystallinity loss. If T_{max} is smaller than T_m, electrical annealing takes place and partially recovers the quenched layered structure, but the melting enthalpy never reaches that of the first pulse. |
| 10 | **Thermochimica Acta 603 (2015), 79-84**  
**Combining TMDSC measurements between chip-calorimeter and molecular simulation to study reversible melting of polymer crystals**  
Xiaoming Jianga, Zhaolei Li, Jing Wang, Huanhuan Gao, Dongshan Zhou, Yuanwang Tang, Wenbing Hu  
**Abstract**  
Reversible melting is a phenomenon unique to polymer crystals, which raises an excess reversing heat capacity near their melting points. By means of temperature-modulated differential scanning calorimetry (TMDSC) measurements with an expanded frequency range in chip-calorimeter, we studied reversing heat capacities of alpha- and beta-form crystals of isotactic polypropylene. We attributed their differences at high temperatures and low frequencies to variable chain mobility in these two crystals. We further performed parallel dynamic Monte Carlo simulations of lattice polymers with variable chain mobility in the crystals to confirm this attribution. Our observations provide the first evidence on the role of chain mobility in the microscopic mechanism of reversible melting at the fold-end surfaces of lamellar polymer crystals. |
Analysis of non-isothermal crystallization during cooling and reorganization during heating of isotactic polypropylene by fast scanning DSC

Jürgen E.K. Schawe

Abstract
Crystallization, reorganization and melting of isotactic polypropylene (iPP) were analyzed by DSC and fast scanning DSC. The cooling and subsequent heating DSC curves are measured at scanning rates between 0.1 K/min and 30,000 K/s. We study the formation of the mesophase and the α-phase during cooling. Using subsequent heating measurements the formation of the mesophase during cold crystallization and the kinetics of the reorganization are analyzed. From the cooling rate dependence of the glass transition and the melting behavior we discuss relations between the crystalline fraction (CF), the mobile amorphous fraction (MAF), the rigid amorphous fraction (RAF) and the influence of these fractions on the reorganization processes. Furthermore, we use the heating rate dependence of the melting behavior for stability analyses of the related crystals and propose the Illers-plot as a simple analysis tool. Using this technique the melting temperature of the mesophase is determined to about 86°C.

Fast cooling of (non)-nucleated virgin and recycled poly(propylenes): Effect of processing conditions on structural and mechanical properties

B.J. Luijsterburg, G.W. de Kort, M. van Drongelen, L.E. Govaert, J.G.P. Goossens

Abstract
In this study, the effect of processing parameters, i.e., the cooling rate and pressure, on the structure-property relationships for nucleated and non-nucleated i-PP from virgin and recycled sources was investigated. Special attention was given to the brittle-to-ductile transition of nucleated i-PP from plastic packaging waste. Differential fast scanning calorimetry and dilatometry were used to mimic industrial process conditions. From the calorimetric experiments, it was observed that under ambient pressure the mesomorphic phase was formed upon fast cooling, which was confirmed by WAXD analysis. The dilatometry results showed that by applying pressure also γ-phase crystals are formed. Nucleated samples showed an increased tendency for the γ-phase formation and a decreased tendency for mesomorphic phase formation. Up to now, recycled i-PP showed a brittle behavior, but this study showed that by applying a sufficiently high cooling rate, the yield stress can be reduced and a stabilization of the deformation can be obtained leading to a ductile behavior for recycled i-PP.
**Thermochimica Acta 603 (2015), 103-109**

**Crystallization kinetics of polyamide 66 at processing-relevant cooling conditions and high supercooling**

*Alicyn Marie Rhoades, Jason Louis Williams, René Androsch*

**Abstract**
Processing of polyamide 66 (PA 66) by injection molding includes cooling of the melt at rates between $10^0$ and $10^3$ K/s and its solidification at high supercooling. The kinetics of crystallization at such conditions is unknown and has been evaluated in this work using fast scanning chip calorimetry. Slow cooling of the melt of PA 66 leads to formation of crystals, with the maximum crystallinity being about 30%. It has been found by analysis of the crystallinity as a function of the cooling rate that crystallization is suppressed on cooling faster than about 300 K/s. Isothermal analysis of the crystallization rate revealed a bimodal temperature dependence, with maxima obtained at about 165 and 11°C. It is suggested that the observation of two distinct crystallization-rate maxima is related to a change of the nucleation mechanism on temperature variation or the formation of different crystal polymorphs exhibiting different growth rate. The findings provide a fundamental step towards accurately predicting the solidification behavior, the skin–core morphology, and properties of injection moldings of PA 66.

**Thermochimica Acta 603 (2015), 110-115**

**Vitrification and crystallization of poly(butylene-2,6-naphthalate)**

*Koji Nishida, Evgeny Zhuravlev, Bin Yang, Christoph Schick, Yasuhiro Shiraishi, Toshiji Kanaya*

**Abstract**
The differential fast scanning calorimetry (DFSC) technique has been successfully applied to study the vitrification and crystallization of poly(butylene-2,6-naphthalate) (PBN). The cooling rate larger than 6000 K/s could make the PBN vitrify and the cooling rate larger than 30,000 K/s reduced effectively the development of the active nuclei. The critical cooling rate of 30,000 K/s is three times as large as that of the recently reported poly(ε-caprolactone) (PCL)'s. Namely, it turned out that PBN is a hard-to-vitrify polymer. The heating rate faster than 7000 K/s could prevent the cold crystallization from the proper glassy state. In the less severe cooling and heating rates than 30,000 K/s and 7000 K/s, respectively, a variety of structure formations, such as the nucleation, the mesophase formation, the crystallization and their multiple melting behaviors, have been observed.
Fast scanning calorimetry study of the structural relaxation in a random propylene-co-1-octene copolymer

Javier Arranz-Andrés, María L. Cerrada, Ernesto Pérez

Abstract
The structural relaxation (or physical aging) has been analyzed by means of fast scanning calorimetry for a random propylene-co-1-octene copolymer, in a wide range of annealing temperatures and times. For annealing temperatures well below \( T_g \) only the structural relaxation is observed and both the rate of enthalpy recovery and the peak temperatures related to the relaxation show a remarkable reduction with decreasing annealing temperatures. When the glass transition temperature is approached, although the structural relaxation is observed first, mesophase ordering is obtained at higher annealing times. The analysis of this mesophase ordering suggests homogeneous nucleation, and, in agreement with prior research in this field, the main feature is that the ordering in the glassy state requires prior completion of the enthalpy relaxation.

Measurement of the limiting fictive temperature over five decades of cooling and heating rates

Siyang Gao, Sindee L. Simon

Abstract
The fictive temperature (\( T_f \)) was defined by Tool in the 1940s as a measure of glassy structure. \( T_f \) is generally measured on heating and can be calculated from the enthalpy overshoot in calorimetric studies using a method developed by Moynihan. Prior work has demonstrated that the limiting fictive temperature (\( T'_f \)) is similar to \( T_g \) (measured on cooling) and depends on the cooling rate in a manner consistent with the Williams–Landel–Ferry (WLF) relationship. Theoretically, the limiting fictive temperature should not depend on heating rate, but this has been experimentally verified only for a very limited range of heating rates. Here, rapid-scanning chip calorimetry and conventional differential scanning calorimetry (DSC) are combined to investigate \( T'_f \) for polystyrene over a broad range of heating rates ranging from 0.017 to 3000 K/s after cooling at different rates. The results show that \( T'_f \) depends on cooling rate following the WLF equation. On the other hand, \( T_f \) is not a function of heating rate, consistent with theoretical predictions, in spite of the change in the magnitude and placement of the enthalpy overshoot.
Measurement of the thermal glass transition of polystyrene in a cooling rate range of more than six decades

Jürgen E.K. Schawe

Abstract
The thermal glass transition of polystyrene (PS) is measured in a range between 0.003 K/s and 4000 K/s using a conventional DSC 1 and a Flash DSC 1 from Mettler-Toledo. The dependency between the cooling rate and the glass transition temperature is in accordance with the Vogel–Fulcher–Tamman–Hesse (VFTH) equation, as it is usually used for description of the frequency–temperature relationship of the dynamic glass transition (or main relaxation process). Furthermore we discuss the influence of the thermal lag on the measurement and develop correction methods.

Structural recovery of a single polystyrene thin film using nanocalorimetry to extend the aging time and temperature range

Yung P. Koh, Luigi Grassia, Sindee L. Simon

Abstract
The structural recovery of a single polystyrene thin film is investigated using nanocalorimetry at aging times as short as 0.01 s, as well as aging at temperatures as high as 15 K above the nominal glass transition temperature for high fictive-temperature glasses obtained at high cooling rates. The results indicate that structural recovery progresses as expected when the aging temperature is low compared to the initial fictive temperature; in this case, the fictive temperature evolves smoothly towards the aging temperature at a rate that depends on the aging temperature and initial fictive temperature (i.e., on the cooling rate prior to aging), and at equilibrium, the fictive temperature $T_f = T_a$. For the case when the aging temperature is much higher than the initial fictive temperature, no relaxation occurs during isothermal aging. For the intermediate case when the aging temperature is in the vicinity of the initial fictive temperature, relaxation occurs both during isothermal aging and during cooling after aging, with the result that the equilibrium fictive temperature is lower than the aging temperature. The use of a new equation for the relaxation time in the framework of the Tool–Narayanaswamy–Moynihan (TNM) model allows description of the data with a single set of model parameters.
Enthalpy relaxation of selenium observed by fast scanning calorimetry

R. Pilar, P. Honcová, G. Schulz, C. Schick, J. Málek

Abstract

The enthalpy relaxation of amorphous selenium was studied using fast scanning calorimeter, where the heating/cooling rates up to 10,000K s\(^{-1}\) were used. The observed relaxation effects were compared with the measurements done by classical differential scanning calorimetry. Description of the data and prediction of the relaxation behavior using the Tool–Narayanaswamy–Moynihan model is discussed.

Reprint of "Heat Capacity and transition behavior of sucrose by standard, fast scanning and temperature-modulated calorimetry"

A. Magoń, A. Wurm, C. Schick, Ph. Pangloli, S. Zivanovic, M. Skotnicki, M. Pyda

Abstract

The heat capacity (\(C_\text{p}\)) of crystalline and amorphous sucrose was determined using standard and quasi-isothermal temperature modulated differential scanning calorimetry. The results were combined with the published data determined by a diabatic calorimetry, and the \(C_\text{p}\) values are now reported for the wide 5–600 K range. The experimental \(C_\text{p}\) of solid sucrose at 5–300 K was used to calculate the vibrational, solid \(C_\text{p}\) based on the vibrational molecular motions. The calculated solid and liquid \(C_\text{p}\) together with the transition parameters for equilibrium conditions were used as references for detailed quantitative thermal analysis of crystalline and amorphous sucrose. Melting temperature (\(T_m\)) of the crystalline sucrose was identified in a broad 442–465 K range with a heat of fusion of 40–46J/mol determined at heating rates 0.5–20 K/min, respectively. The equilibrium \(T_m\) and heat of fusion of crystalline sucrose were estimated at zero heating rate as \(T_m = 424.4\) K and \(\Delta H_f = 32kJ/mol\), respectively. The glass transition temperature (\(T_g\)) of amorphous sucrose was at 331 K with a change in \(C_\text{p}\) of 267J/(mol K) as it was estimated from reversing heat capacity by quasi-isothermal TMDSC on cooling. At heating rates less than 30K/min, thermal decomposition occurred during melting,while at extreme rate of 1000K/s, degradation was not observed. Data obtained by fast scanning calorimetry (FSC) at 1000 K/s, showed that \(T_m\) was 483 K and \(T_g\) was 364 K. Super heating effects were observed during the melting with the maximum value around 46 K at 1000 K/s.
Fast differential scanning calorimetry of liquid samples with chips

R. Splinter, A.W. van Herwaarden, I.A. van Wetten, A. Pfreundt, W.E. Svendsen

Abstract
Based on a modified version of standard chips for fast differential scanning calorimetry, DSC of liquid samples has been performed at temperature scan rates of up to 1000 °C/s. This paper describes experimental results with the protein lysozyme, bovine serum, and olive oil. The heating and cooling rate of the sensor is measured for temperature scan rates of up to 1300 °C/s with water and 2-butanol, in the temperature range of -90 °C/s to +130 °C/s. The lysozyme is measured at temperature scan rates varying from 10 °C/s to 400 °C/s and in concentrations between 0.1% and 10% protein by weight. The bovine serum measurements show two main peaks, in good agreement with standard DSC measurements. Olive oil has been measured, with good agreement for the cooling curve and qualitative agreement for the heater curve, compared to DSC measurements.

Toward high-throughput chip calorimetry by use of segmented-flow technology


Abstract
The adaptation of segmented-flow technology to flow-through calorimetry was demonstrated by different kinds of newly designed chip calorimeters useful for liquids and suspensions as well as for solid samples. In segmented-flow technology, sample material is suspended in aqueous segments of nan-liter or microliter volume and transported by a water-immiscible carrier liquid. The analysis of the signal dynamics given by segmented samples in flow led to optimal settings of flow rate and sample volume for maximal throughput. For 12 µL sample segments, a cycle time of 4 min could be achieved. The protection of the measuring chamber of the calorimeters against biofouling caused by the water-immiscible carrier liquid was verified for segmented bacterial samples. The unique possibility to measure solid and aggregated samples in flow-through was demonstrated by the investigation of human hair follicles and fibroblast spheroids.
A continuous flow microfluidic calorimeter: 3-D numerical modeling with aqueous reactants

Mehmet A. Sen, Gregory J. Kowalski, Jason Fiering, Dale Larson

Abstract
A computational analysis of the reacting flow field, species diffusion and heat transfer processes with thermal boundary layer effects in a microchannel reactor with a coflow configuration was performed. Two parallel adjacent streams of aqueous reactants flow along a wide, shallow, enclosed channel in contact with a substrate, which is affixed to a temperature controlled plate. The Fluent computational fluid dynamics package solved the Navier–Stokes, mass transport and energy equations. The energy model, including the enthalpy of reaction as a nonuniform heat source, was validated by calculating the energy balance at several control volumes in the microchannel. Analysis reveals that the temperature is nearly uniform across the channel thickness, in the direction normal to the substrate surface; hence, measurements made by sensors at or near the surface are representative of the average temperature. Additionally, modeling the channel with a glass substrate and a silicone cover shows that heat transfer is predominantly due to the glass substrate. Finally, using the numerical results, we suggest that a microcalorimeter could be based on this configuration, and that temperature sensors such as optical nanohole array sensors could have sufficient spatial resolution to determine enthalpy of reaction.

Reprint of “An evaluation of thermal lags of fast-scan microchip DSC with polymer film samples”

Akihiko Toda, Misuzu Konishi

Abstract
A quantitative evaluation has been tried on the thermal lags of a fast-scan ($< 10^4$ Ks$^{-1}$) microchip differential scanning nanocalorimeter (DSC). At thin layer ($\sim 0.2$ µm thick) of a standard material of Tin was vapor deposited on a thin film of polyethylene (PE) sample ($\sim 1$–$10$ µm thick), and the thermal lags have been examined by the dependences on the applied heating rate, film mass, and film thickness of the melting onset temperature of Tin on the bottom and top surfaces of PE films put on the sensor stage of nanocalorimeter. Thermal lags are comprised of the instrumental thermal resistance and the temperature gradient in the film. The instrumental thermal lag was detected by the melting of Tin on the bottom of PE films and well explained by the reported value of the thermal resistance of sensor. The temperature gradient in the film was detected by the melting of Tin on the top surface of PE films, and showed the dependence predicted by the modeling of heat transfer in the thickness direction. The influences of thermal lags have also been examined in terms of the heating rate, $\beta$, dependence of the shift in melting peak temperature of PE crystals. The power of $\beta$ characterizing the $\beta$ dependence of the shift became larger within decreasing film mass and thickness, i.e. with introducing larger thermal lags. When the power is utilized as a fitting parameter, the influence of thermal lags on the melting point extrapolated to zero heating rate could be kept at small level ($\pm 1 \degree C$) even for thick films ($\sim 10$ µm). Those behaviors have been validated by numerical calculations based on the modeling of fast-scan microchip DSC.
Dynamics of the temperature distribution in ultra-fast thin-film calorimeter sensors

Alexander A. Minakov, Christoph Schick

Abstract
To study phase-transition kinetics on submillisecond time scales a set of thin-film silicon–nitride gauges for ultra-fast scanning nanocalorimetry was constructed and utilized for controlled ultra-fast cooling, as well as heating, up to 106 K/s. In this paper an analytical solution for the model describing the heat transfer in a membrane gauge at ultra-fast heating and cooling is presented. The dynamics of the temperature distribution in the membrane gauge is calculated and compared with experimental data. The origin of limitations imposed on the maximum attainable controlled cooling rate is investigated.

Thermocouples, their characteristic temperatures, and simple approximation of the emf vs. T

V.A. Drebushchak

Abstract
Calibration of the temperature and heat flux sensors for chip calorimetry is more effective if it is based on the optimal approximation of thermocouple's emf against temperature. Contact theory of thermoelectricity provides us with the formula for the approximation, but implies the characteristic temperature of a thermocouple constant $\Theta_v$. This assumption turned out to be incorrect in common practical use, what did makes the main problem for the approximation of the emf. At the same time, the theory explains that the rate of increase for the emf with temperature is not greater than $T^2$. Three-point tests with the reference tables of type E and S thermocouples and many-point test with experimental data did not reveal evident preference of one procedure of approximation over the others. In considering all circumstances of the approximation, the 2nd-order polynomial is concluded to be the best way to approximate the emf of a thermocouple for practical use. Approximation of the characteristic temperature of type E thermocouple with square polynomial $277.01 - 0.63453 T + 0.00044352 T^2$ results in the accuracy of ±0.5 K over the temperature range from 0 to 1000°C.
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Temperature modulated differential scanning calorimetry – extension to high and low frequencies

Evgeni Shoifet, Gunnar Schulz, Christoph Schick

Abstract
Common temperature modulated DSCs are limited in the accessible frequency range to about 0.1–0.001 Hz. We describe an extension of this frequency range towards lower and higher frequencies by using conventional DSCs (without TMDSC option). By applying steps in the temperature-time profile a simultaneous multi frequency analysis of the heating rate and the heat flow rate response yields heat capacity data over about 2 orders of magnitude in frequency from one single measurement. Based on this step response analysis we show on the example of a Calvet calorimeter, Setaram BT 2.15, an extension down to $10^{-5}$ Hz and on the example of a chip calorimeter, Mettler Toledo Flash DSC 1, an extension up to 150 Hz. Details of the experimental procedures are provided and the influence of sample size on the obtained data and general limitations, particularly regarding temperature assignment, are discussed. A relaxation map is used to combine all calorimetric data and to compare them with dielectric data.

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Detection of sunflower oil in extra virgin olive oil by fast differential scanning calorimetry

I.A. van Wetten, A.W. van Herwaarden, R. Splinter, R. Boerrigter-Eenling, S.M. van Ruth

Abstract
Extra virgin olive oil (EVOO) is an economically valuable product, due to its high quality and premium price. Therefore it is vulnerable for adulteration by means of the addition of cheaper vegetable oils. Differential scanning calorimetry (DSC) has been suggested as a fast technique for the detection of adulteration. However, measurements still take several hours. Fast DSC measurements take several minutes. Therefore this study investigates the applicability of fast DSC for the detection of sunflower oil (SFO) in EVOO. Nine EVOOs, five SFOs and three mixtures were analysed. Cooling curves of EVOO and SFO show one major exothermic peak. Because the cooling curves of EVOO and SFO are very similar they cannot be used for the detection of adulteration. Heating curves of EVOOs show two major endothermic peaks after slow cooling (-2 °C/s), heating curves of SFOs only one. Addition of SFO to EVOO caused a rapid decrease in the coldest endothermic peak and can therefore be used in the detection of adulteration of EVOO by SFO. Depending on the type of olive oil, the presence of 2–10% SFO can already be detected.
**New design of a microcalorimeter for measuring absolute heat capacity from 300 to 550 K**

Woong-Jhae Lee, Hyung Joon Kim, Jae Wook Kim, Dong Hak Nam, Ki-Young Choi, Kee Hoon Kim

**Abstract**

We report development of a new type of a microcalorimeter based on an amorphous membrane composed of Si:N and SiO$_2$ layers, which holds an isothermal Au film of a disc shape and concentric Pt leads as a heater and a thermal sensor. Two-dimensional thermal simulation was used to confirm that the layout of the isothermal platform and metallic leads result in nearly perfect isothermal conditions at temperatures from 20 to 600 K. Moreover, by placing the insulating SiO$_2$ layer between the isothermal film and metallic leads, we could locate all electrical and thermal components in the top side of the membrane, allowing the micro-fabrication easy and cost-effective. The micro-fabrication method produces a total of 49 devices in a four inch Si wafer and can be also applied in a larger wafer size. Heat capacity value of the isothermal platform was found to be as small as $\sim 6\mu$J K$^{-1}$ at room temperature. Upon applying the lumped-$\tau$ model in the measurement scheme, we found that specific heat of an Al$_2$O$_3$ single crystal (NIST standard, $\sim 0.2$ mg) was consistent with the literature value within $\sim 3\%$ at temperatures between 300 and 550 K. Our results show that the circular layout of the isothermal platform with better heat confinement is useful for increasing the accuracy of measured heat capacity if the other parameters such as thickness and thermal conductivity of each layer in the membrane are fixed.

**Comparing crystallization rates between linear and cyclic poly(epsilon-caprolactones) via fast-scan chip-calorimeter measurements**

Jing Wang, Zhaolei Li, Ricardo A. Pérez, Alejandro J. Müller, Boyu Zhang, Scott M. Grayson, Wenbing Hu

**Abstract**

The vital role of chain ends in the crystallization of linear polymers can be understood by unraveling the mechanisms of crystallization of cyclic polymers. A commercial chip-calorimeter Flash DSC1 was employed to compare the nucleation and overall crystallization rates between linear and cyclic poly(epsilon-caprolactones) (PCL) with similar molar masses of around 2 kg/mol. In the high temperature region, faster overall crystallization of cyclic PCL relative to linear PCL is consistent with previously reported results employing conventional DSC. In the low temperature region, the cyclic PCL exhibits a lower onset temperature of homogenous nucleation when compared to linear PCL analogs. This result was attributed to a higher mobility of free chain ends in the linear PCL as compared to cyclic PCL. A simplified data-treatment method on the nucleation half-time has been proposed.
**Polymer 55 (2014), 5255-5265**

**Crystallization behavior and morphological characterization of poly(ether ether ketone)**

*Lin Jin, Jerry Ball, Tim Bremner, Hung-Jue Sue*

**Abstract**
The crystal structure and morphology of poly(ether ether ketone) (PEEK) was investigated using standard differential scanning calorimetry (DSC), flash DSC, optical microscopy, atomic force microscopy, and small angle X-ray scattering tools. The flash DSC results suggested that the double melting peaks phenomenon observed in conventional DSC work originated from the reorganization of PEEK crystals, which was due to the much faster recrystallization rate of PEEK than the DSC heating and cooling rate. A refined crystallization model to describe PEEK crystal structure formation was proposed. The refined crystallization model could help reconcile the discrepancy found between the bulk crystallinity measured by DSC and the linear crystallinity obtained from SAXS experiments by taking into account possible variation in crystal perfection within the lamellar structure. Simplified molecular dynamic modeling was carried out to support this model. Implications of the above findings to the fundamental understanding of structure-property relationships in PEEK were discussed.

**Thermochimica Acta 615 (2015), 8-14**

**Using flash DSC for determining the liquid state heat capacity of silk fibroin**

*Peggy Cebe, Benjamin P. Partlow, David L. Kaplan, Andreas Wurm, Evgeny Zhuravlev, Christoph Schick*

**Abstract**
In this technical note, we report a study of the heat capacity of amorphous silk fibroin protein evaluated using the Flash DSC1 for fast scanning calorimetry. Nineteen amorphous thin films were obtained either after casting directly from water solutions, or after melting of previously crystalline films. Fibroin films were mounted onto Flash DSC1 sensors, dried free of bound water, relaxed just above the glass transition, $T_g$, then scanned in heating and cooling at ±200 K/s. The heat flow rate data were analyzed by finding the symmetry line between the heating and cooling scans, and by subtraction of the empty sensor heat flow rate, similarly corrected for its symmetry line. To evaluate the sample mass, two approaches were compared. First, the mass was obtained from known solid state heat capacity, $C_p^{\text{solid}}(T)$, at a temperature below $T_g$. Second, the mass was obtained from the known heat capacity increment at the glass transition, $\Delta C_p(T_g)$. The $C_p^{\text{solid}}(T)$ and $\Delta C_p(T_g)$ had been obtained previously from slow scanning differential scanning calorimetry. The use of either method for mass determination necessitated additional corrections to the heat capacity data to bring them into agreement with the literature values. After these corrections, the heat capacity of silk fibroin in the liquid state was evaluated over a wide temperature range above $T_g$. We find $C_p^{\text{liquid}}(T) = (1.98 \pm 0.06)$ J/gK + $T^{-1} (6.82 \pm 1.4) \times 10^{-4}$ J/gK² in the temperature interval from 510 to 570 K with an uncertainty of about ±5%.
Two processes of $\alpha$-phase formation in polypropylene at high supercooling

Jürgen E.K. Schawe, Paul A. Vermeulen, Martin van Drongelen

Abstract
The non-isothermal and isothermal crystallization of different types of commercial polypropylenes (PP) are investigated by fast scanning calorimetry and wide-angle X-ray scattering. Typically, PP shows two different crystallization processes: below 55°C the mesophase formation and at higher temperatures the $\alpha$-phase formation. Here we report the first observation of an additional crystallization process in some PP-types. It is observed between 45°C and 75°C, and is understood as a consequence of an additional nucleation of $\alpha$-phase crystals.

Density of heterogeneous and homogeneous crystal nuclei in poly (butylene terephthalate)

René Androsch, Alicyn Marie Rhoades, Isabell Stolte, Christoph Schick

Abstract
Quantitative analysis of the nucleation density of poly (butylene terephthalate) using microscopy yielded values of $10^6$ and $10^{15}$ nuclei mm$^{-3}$ for the cases of heterogeneous and homogenous nucleation on crystallization at low and high supercooling of the melt, respectively. Fast scanning chip calorimetry revealed that the largely different nucleation densities cause two crystallization-rate maxima at 130 and 70°C, with characteristic minimum crystallization times of the high- and low-temperature crystallization processes being about 1 and 0.1 s, respectively. It has furthermore been excluded by X-ray scattering that the low-temperature crystallization-rate maximum is due to the formation of a different crystal polymorph; independent of the supercooling there is observed formation of $\alpha$-crystals. The crystallization study has been completed by analysis of the non-isothermal crystallization behavior, identifying a minimum critical cooling rate of about 10 K s$^{-1}$ to avoid completion of the high-temperature crystallization process and to initiate crystallization at low temperature. For complete vitrification, the PBT melt needs to be cooled faster than 200 K s$^{-1}$. 
Form I’ crystal formation in random butene-1/propylene copolymers as revealed by real-time X-ray scattering using synchrotron radiation and fast scanning chip calorimetry

Isabell Stolte, Dario Cavallo, Giovanni C. Alfonso, Giuseppe Portale, Martin van Drongelen, René Androsch

Abstract
The crystallization behavior of random isotactic butene-1/propylene copolymers has been investigated as a function of the propylene concentration and as a function of the crystallization temperature in a wide temperature range from 273 to 343 K, with emphasis placed on the detection of formation of Form I’ crystals. Form I’ crystals in random butene-1/propylene copolymers develop if the propylene content is larger than about 10 mol%. For a random butene-1/propylene copolymer with 11.4 mol% propylene it was found that Form I’ crystals only form below 310 K, with the relative amount increasing with decreasing crystallization temperature. A maximum Form I’ crystal fraction of about 1/3 of the total crystal fraction has been observed on crystallization at 273 K. Regardless the temperature of its formation, the thermal stability of metastable Form I’ crystals is distinctly lower than the thermal stability of unstable Form II mesophase and stable Form I crystals, if formed at identical temperature.

Effect of an alpha-phase nucleating agent on the crystallization kinetics of a propylene/ethylene random copolymer at largely different supercooling

René Androsch, Andrea Monami, Jaroslav Kucera

Abstract
The effect of addition of 0.1 wt% phosphate-ester based alpha-phase nucleating agent on the crystallization of a random propylene-based copolymer with 3.9 mol% ethylene has been investigated by fast scanning chip calorimetry (FSC). Main purpose of the work was the evaluation of the effect of the nucleating agent on the bimodal temperature dependence of the crystallization rate of propylene-based polymers caused by a change of the nucleation mechanism from heterogeneous to homogeneous nucleation on lowering the temperature to below about 60°C. Presence of the nucleation agent in the copolymer of the present study accelerates crystallization only in the high-temperature range of predominant heterogeneous nucleation, but does not affect the crystallization rate in the low-temperature range of homogeneous nucleation. The observed decrease of the minimum crystallization half-time due to the addition of the nucleation agent, from 0.2 s in case of the unmodified copolymer to 0.04 s in case of the copolymer containing the nucleating agent, is paralleled by an increase of the critical cooling rate required to inhibit crystallization on continuous cooling to below the glass transition temperature from $10^5$ to $10^3$ K s$^{-1}$. The study is completed by an analysis of the effect of addition of the nucleation agent on the spherulitic superstructure.
Kinetic competition during glass formation

J.H. Perepezko, C. Santhaweesuk, J.Q. Wang, S.D. Imhoff

Abstract
For vitrification of an alloy melt during cooling there is a kinetic competition with the nucleation and growth of metastable and stable crystalline phases. Many of the measures of glass forming ability (GFA) attempt to capture some of the features of the kinetic competition, but the GFA metrics are static measures and the kinetic processes are dynamic in nature. In fact, the critical cooling rate for glass formation should be viewed in terms of a critical cooling rate range to acknowledge the stochastic nature of crystal nucleation behavior. Direct measurements of the critical cooling rate range confirm this behavior and also provide useful input for kinetics analysis. Usually kinetics analyses are based upon crystallization behavior that is measured either isothermally or upon heating to temperatures near the crystallization onset, $T_x$ and the results are extrapolated to much higher temperatures. This practice is based upon a number of assumptions about transport behavior in the undercooled liquid. With rapid up-quenching of amorphous samples, the high temperature crystallization behavior can be measured and used to refine the kinetics analysis and provide useful insight on the kinetic competition and glass forming ability.

Solid-state reorganization, melting and melt-recrystallization of conformationally disordered crystals ($\alpha'$-phase) of poly (L-lactic acid)

René Androsch; Evgeny Zhuravlev; Christoph Schick

Abstract
Conformationally disordered $a_0$-crystals of poly (L-lactic acid) were formed by crystallization of the melt at high supercooling at 95 °C. Analysis of their melting temperature as a function of the crystallinity revealed absence of crystal thickening during isothermal crystallization. Annealing of $\alpha'$-crystals between the crystallization temperature of 95 °C and their zero-entropy production melting temperature of 150 °C leads to their stabilization, mainly by solid-state reorganization. Heating faster than 30 K s$^{-1}$ suppresses reorganization and permits superheating of the $\alpha'$-phase. Consequently, isothermal melting followed by melt-recrystallization becomes accessible. Melting is completed within few hundreds of milliseconds, and melt-recrystallization is about two orders of magnitude faster than crystallization of the isotropic melt at identical temperature. The time required for melting decreases with superheating and increases with the lateral dimension of the lamellar crystals. Laterally extended lamellae require long time for melting of the outer crystal layers, which allows stabilization of the central crystal part. These crystal remnants then serve as seed for immediate recrystallization. In case of complete melting of smaller lamellae, melt-recrystallization is retarded but still distinctly faster than cold- and melt-crystallization, due to incomplete isotropization of the melt.
Unusual crystallization behavior of isotactic polypropylene and propene/1-alkene copolymers at large undercoolings


Abstract
During the investigation of the crystallization of metallocene isotactic polypropylene and copolymers with low amount of 1-butene and 1-hexene at large undercoolings, an unexpected behavior has been found. Random copolymers crystallize faster than the homopolymer between 80 and 40 °C, while at high temperatures the overall crystallization rates follow the expected trend. On the basis of structural and morphological evidences we suggest that the overall structuring kinetics of the homopolymer is slowed down by the concomitant formation of mesophase and monoclinic structures. This effect is absent in the copolymers because the branched counits retard the development of mesophase.

Combining fast-scan chip-calorimeter with molecular simulations to investigate superheating behaviors of lamellar polymer crystals

Huanhuan Gao, Jing Wang, Christoph Schick, Akihiko Toda, Dongshan Zhou, Wenbing Hu

Abstract
We studied the power-law heating-rate dependence of superheating for the melting of alpha- and betacrystals of isotactic polypropylene by means of chip-calorimeter, and expanded our parallel observation to higher heating rates by means of molecular simulations. We observed that, at low heating rates, the melting of lamellar crystals after thickened via melting-recrystallization exhibits no power-law-dependent superheating; at medium heating rates, the melting of crystals after thickened via chainsliding diffusion exhibits the power-law-dependent superheating with the power indexes sensitive to chain mobility in the crystals; while at high heating rates, the zero-entropy-production melting of crystals without further thickening maintains the power-law-dependent superheating but with the power indexes uniform at an upper-limit 0.375. We attributed the index 0.375 to a result combining local intramolecular nucleation and global roughening growth at the lateral surface of lamellar crystals, which dominate the kinetics of crystal growth and melting of polymer crystals at high temperatures.
**Study of melting and crystallization behavior of polyacrylonitrile using ultrafast differential scanning calorimetry**

Yoshitomo Furushima, Masaru Nakada, Hideaki Takahashi, Kazuhiro Ishikiriyama

**Abstract**
The thermal behavior of polyacrylonitrile (PAN) has been investigated using X-ray diffraction, differential scanning calorimetry (DSC), and ultrafast DSC. In conventional DSC, it is difficult to prevent the concurrent occurrence of the exothermic reactions of PAN with melting. However, in the ultrafast DSC curve, the exothermic peak due to these reactions disappears over the temperature range 0-400 °C at heating rates above 250 °C s⁻¹. Alternatively, the glass transition and the melting of PAN are observed over the temperature range 109-129 °C and 335-362 °C, respectively. Moreover, upon cooling from the molten state at a rate of -7500 °C s⁻¹, PAN crystallization is observed at 204 °C. These findings were observed repeatedly during heating and cooling measurements. From the extrapolation analysis, the zero-entropy production melting temperature of PAN is found to lie in the temperature range 320-350 °C. Finally, the equilibrium melting temperature of PAN is estimated to be ca. 465 °C.

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**The ultrastable kinetic behavior of an Au-based nanoglass**


**Abstract**
Ultrastable glasses and nanoglasses are two emerging materials with novel properties that have been investigated separately. In order to explore the combined effect of ultrastable character and a nanoglass with a nanoglobular microstructure on the kinetic behavior, the glass transition and crystallization behaviors of an ultrastable nanoglass and a melt-spun ribbon of Au-based metallic glass were examined by differential scanning calorimetry at heating rates of up to 40,000 K s⁻¹. The nanoglass shows ultrastable kinetic characters at low (e.g. 300 K s⁻¹) and similar kinetic behaviors at high (e.g. 30,000 K s⁻¹) compared to the melt-spun ribbon. The nanoglobular interfaces remain amorphous and appear to act as a kinetic constraint to induce a higher crystallization temperature compared to the melt-spun ribbon. The interface constraint effect disappears at 30,000 K s⁻¹. These results indicate that the nanoglobular microstructure can act to increase metallic glass stability and provide another mechanism for the synthesis of ultrastable glass.
Sequence of enthalpy relaxation, homogeneous crystal nucleation and crystal growth in glassy polyamide 6

René Androsch; Christoph Schick; Jürn W.P. Schmelzer

Abstract
The sequence of densification/enthalpy relaxation, crystal nucleation and crystal growth in glassy polyamide 6 has been quantified using fast scanning chip calorimetry. The melt was vitrified by fast cooling, and then the glass was annealed as a function of temperature and time, covering a time scale of six orders of magnitude, required to separate the individual relaxation/ordering processes. During annealing of the glass, there is first observed enthalpy relaxation, and only after its completion there is detected crystal nucleation followed by crystal growth. A homogeneous nucleation mechanism is suggested. In such case, the characteristic relaxation time of the glass to attain metastability, that is, of its densification, has been shown theoretically (Gutzow and Schmelzer, 2013) to be as a rule much shorter than the characteristic time of nucleus formation.

Using Flash DSC Technology to Verify Structural Changes

Jürgen E. K. Schawe; Andreas Köhler

Abstract
With semi-crystalline polymers, structural differences determine a product’s mechanical properties. The example of extruded tubes is used to describe how the recently developed Flash DSC technology is applied to examine the influence of individual production stages on material structures.

Experimental study of crystallization of PolyEtherEtherKetone (PEEK) over a large temperature range using a nano-calorimeter

Xavier Tardif; Baptiste Pignon; Nicolas Boyard; Jürn W.P. Schmelzer; Vincent Sobotka; Didier Delaunay; Christoph Schick

Abstract
The recently developed fast scanning differential calorimetry is used for the first time to determine the crystallization kinetics of Poly(EtherEtherKetone) (PEEK). In our experiments, crystallization is studied in isothermal conditions over a large temperature range from 170 °C to 310 °C. Two different measurement protocols were employed. Between 200 °C and 300 °C the heat flow was directly measured during isothermal crystallization. Outside this temperature range we measured the heat of fusion on heating after interrupted isothermal crystallization. We show that data can be analyzed with the Avrami approach incorporating a term describing secondary crystallization. The crystallization half-times are measured. The Avrami kinetic coefficient $K_A$ associated with primary crystallization is evaluated from isothermal crystallization between 170 °C and 310 °C where data were not previously available. The kinetics of crystallization of PEEK has only one maximum located around 230 °C and its Avrami exponent is close to 3, suggesting instantaneous nucleation with subsequent spherical growth. The whole isothermal crystallization process is modeled in terms of Hillier’s model since it takes secondary crystallization kinetics into account. Finally, it is shown that the double melting peak behavior observed after isothermal crystallization (below 260 °C) is a consequence of the reorganization process during heating.
Combining TMDSC measurements between chip-calorimeter and molecular simulation to study reversible melting of polymer crystals

Xiaoming Jiang; Zhaolei Li; Jing Wang; Huanhuan Gao; Dongshan Zhou; Yuanwang Tang; Wenbing Hu

Abstract

Reversible melting is a phenomenon unique to polymer crystals, which raises an excess reversing heat capacity near their melting points. By means of temperature-modulated differential scanning calorimetry (TMDSC) measurements with an expanded frequency range in chip-calorimeter, we studied reversing heat capacities of alpha- and beta-form crystals of isotactic polypropylene. We attributed their difference at high temperatures and low frequencies to variable chain mobility in these two crystals. We further performed parallel dynamic Monte Carlo simulations of lattice polymers with variable chain mobility in the crystals to confirm this attribution. Our observations provide the first evidence on the role of chain mobility in the microscopic mechanism of reversible melting at the fold-end surfaces of lamellar polymer crystals.

Kinetics of crystal nucleation of poly(L-lactic acid)

René Androsch; Maria Laura Di Lorenzo

Abstract

The kinetics of crystal nucleation of poly(L-lactic acid) (PLLA) has been analyzed by fast scanning chip calorimetry in a wide temperature range between 313 and 383 K, that is, between temperatures about 30 K below and 40 K above the glass transition temperature. The relaxed melt was rapidly cooled to the analysis temperature and subsequently aged between $10^1$ and $10^4$ s, to permit formation of nuclei. The number of formed crystal nuclei has been probed by analysis of the crystallization rate at 393 K. The nucleation rate is maximal at 370-375 K and decreases monotonously with decreasing temperature in the analyzed temperature range. The observation of a monomodal dependence of the nucleation rate on temperature points to predominance of a single nucleation mechanism in the analyzed temperature range, regardless nucleation occurs in the glassy or devitrified amorphous phase. The collected data suggest that nuclei formation at ambient temperature requires a waiting time longer than about $10^8$ s. The performed study is considered as a quantitative completion of nucleation-rate data available for PLLA only at temperatures higher than 360 K, suggesting that the nucleation mechanism is independent on temperature in the analyzed temperature range between 313 and 383 K.
Kinetics of the melt e Form II phase transition in isotactic random butene-1/ethylene copolymers

Isabell Stolte, René Androsch

Abstract

The kinetics of formation of the Form II mesophase from the melt has been investigated as a function of the concentration of ethylene chain defects in isotactic random butene-1/ethylene copolymers, using standard and fast scanning chip calorimetry. Presence of ethylene co-units in the butene-1 chain leads to a distinct reduction of the melt e Form II phase transformation rate which has been quantified by evaluation of the critical cooling rate to suppress ordering, and by isothermal analysis of half-times of Form II mesophase formation. For the first time, the temperature-dependence of the rate of Form II mesophase formation has been evaluated for butene-1/ethylene random copolymers and the butene-1 homopolymer. This study needs to be considered as a complementary addendum to former work about the Form II to Form I polymorphic transformation in isotactic random butene-1/ethylene copolymers.

Microfocus wide-angle X-ray scattering of polymers crystallized in a fast scanning chip calorimeter

Martin van Drongelen, Tamara Meijer-Vissers, Dario Cavallo, Giuseppe Portale, Geert Van den Poel, René Androsch

Abstract

Microfocus wide-angle X-ray scattering (WAXS) has been applied for analysis of the polymorphism of isotactic polypropylene and polyamide 6 prepared in a fast scanning chip calorimeter (FSC). Samples with a typical mass of few hundred nanograms, and lateral dimension and thickness of about 100 mm and 20 mm, respectively, were exposed to a defined thermal history in the FSC and subsequently analyzed regarding the X-ray structure at ambient temperature using an intense synchrotron microfocused X-ray beam. The relaxed melt of isotactic polypropylene was cooled at rates of 40 K s$^{-1}$ and 200 K s$^{-1}$ which allowed formation of $\alpha$-crystals or mesophase, respectively. Polyamide 6 was isothermally crystallized at 95 $^\circ$C and 180 $^\circ$C which led to formation of $\gamma$-mesophase and $\alpha$-crystals, respectively. This study demonstrated, for the first time, that FSC polymer crystallization experiments could be completed and expanded by subsequent in situ structure analysis by X-ray scattering.
Calorimetric Glass Transition of Single Polystyrene Ultrathin Films

Siyang Gao, Yung P. Koh, and Sindee L. Simon

Abstract
The calorimetric glass transition (Tg) is measured for single polystyrene ultrathin films using a commercial rapid-scanning chip calorimeter as a function of cooling rate and film thickness. Films have been prepared in two ways: spin-cast films placed on a layer of inert oil or grease and films directly spin-cast on the back of the calorimetric chip. For the films on oil or on grease, the 160 nm thick films show results consistent with those of a bulk sample measured by conventional DSC. On the other hand, the 47 nm thick film on oil and 71 nm thick films both on oil and on grease show a Tg depression which decreases with increasing cooling rate; the magnitude of the Tg depression is similar to results reported in the literature for the most mobile substrate-supported films. For films directly spin-cast onto the sensor, a Tg depression is not observed for 47 and 71 nm thick films but is observed for a 16 nm thick film. These results are also within the range of the data on supported films in the literature but show a smaller depression than films on oil or grease. The effect of annealing is also investigated. For thick films and those directly spin-cast onto the sensor, annealing at 160 °C has no influence on heat flow curves; hence, Tg values remain unchanged. For the 47 and 71 nm thick films on either oil or grease, the depressed Tgs revert to the bulk values over the course of a day at 160 °C. Atomic force microscope (AFM) images show that annealing results in dewetting of the films with hole growth and thickening of the film to 200 nm, the latter of which is presumed to be the reason that Tgs revert to bulk values.

Comprehensive high temperature two-dimensional liquid chromatography combined with high temperature gradient chromatography-infrared spectroscopy for the analysis of impact polypropylene copolymers

Sadiqali Cheruthazhekatt; Gareth W. Harding; Harald Pasch

Abstract
Impact polypropylene copolymers (IPC) are extremely complex materials that can only be effectively analysed by multidimensional analytical approaches. IPC consists of isotactic polypropylene (iPP) as the major phase, ethylene–propylene (EP) copolymers of various compositions and small amounts of polyethylene. The molecular heterogeneity of two IPC samples having different ethylene contents was studied by using a novel cross-fractionation technique, developed from a combination of various analytical separation methods into an effective characterisation tool for complex polyolefins. The initial step involves the fractionation of the sample into EP rubber, EP segmented copolymer, and iPP, by preparative temperature rising elution fractionation (TREF). The resulting fractions are still distributed with regards to chemical composition and molar mass. The separation with respect to these parameters is conducted by comprehensive HT 2D-LC. This is the first time that the individual components in all TREF fractions of an IPC are separated and analysed multidimensionally, by both SEC-FTIR, high-temperature (HT) HPLC-FTIR, and HT 2D-LC. Molar mass analysis of the chemically homogeneous fractions from HT HPLC is accomplished by HT SEC in the second dimension of HT 2D-LC. The chemical composition of all species is determined by coupling FTIR spectroscopy to HT HPLC via an LC-transform interface. This novel approach reveals the capability of this hyphenated technique to determine the exact chemical composition of the individual components in the complex TREF fractions of IPCs. The HT HPLC-FTIR results confirm the separation mechanism in the given chromatographic system using a 1-decanol to TCB solvent gradient and a Hypercarb stationary phase. The components of differing chemical composition are separated according to the nature and length of the propylene/ethylene segments, with their arrangement in the chains strongly affecting their adsorption/desorption on the stationary phase. FTIR analysis provides information on the ethylene and propylene contents of the fractions as well as on the ethylene and propylene crystallinities.
Nonisothermal Crystallization of Polytetrafluoroethylene in a Wide Range of Cooling Rates
Nicolas Bosq, Nathanael Guigo, Evgeny Zhuravlev, Nicolas Sbirrazzuoli

Abstract
Compared to other semicrystalline polymers, PTFE demonstrates a very fast crystallization process on cooling. This study explores for the first time the nonisothermal PTFE ultrafast crystallization under tremendously fast cooling rates (up to 800'000 K·s⁻¹) achieved by using fast scanning calorimetry (FSC) and ultra-fast scanning calorimetry (UFSC). Regular DSC was also used to get crystallization at slower rates. The data obtained on a wide range of cooling rates (over 8 orders of magnitudes) help to get new knowledge about crystallization kinetics of PTFE. Both FSC and UFSC data show that it is impossible to bypass the crystallization and thus to reach a metastable glassy state even for the fastest cooling rate employed (800'000 K·s⁻¹). The crystals formed under such conditions are slightly less stable than those produced under slower cooling rates, as reflected by a shift of the melting peak to lower temperature. The difference in crystal morphologies was confirmed by SEM observations. The variation of the effective activation energy (Eα) with the relative extent of crystallization reveals that PTFE crystallization follows a transition from regime II to regime III around 315−312 °C. Corroborated temperature dependences of Eα obtained respectively for crystallizations under slow and fast cooling rates were combined and fitted to the theoretical dependence of the growth rate derived from the Hoffman−Lauritzen theory.

Melting kinetics of it-polypropylene crystals over wide heating rates
Akihiko Toda, Ken Taguchi, Kano Sato, Koji Nozaki, Masanori Maruyama, Katsuharu Tagashira, Misuzu Konishi

Abstract
Melting kinetics of it-polypropylene crystals has been examined over wide heating rates of 0.6 K min⁻¹−10⁴ K s⁻¹ using a standard DSC and a fast-scan DSC. With fast-scan DSC, we have an access to the melting of crystals obtained at low temperatures, which are susceptible to re-organization at the heating rates applicable with standard DSC. It is clearly discernible that the appearance and disappearance of multiple melting peaks are strongly influenced by the applied heating rates and dependent on the crystallization temperatures. By examining the heating rate dependence of superheating of melting, we have determined the melting points of as-grown crystals formed under wide crystallization temperatures.
Crystallization of isotactic polypropylene containing beta-phase nucleating agent at rapid cooling

Ayret Mollova, René Androsch, Daniela Mileva, Markus Gahleitner, Sergio S. Funari

Abstract
The crystallization behavior of isotactic polypropylene containing a β-phase nucleating agent has been investigated, focusing on evaluation of the effects of cooling rate and/or supercooling of the melt on the generation of different polymorphs. It has been found that β-crystals only form on cooling the melt at rates lower than about 50 K s\(^{-1}\) while cooling at rates between 50 and 300 K s\(^{-1}\) leads to formation of α-crystals; even faster cooling is connected with mesophase formation or vitrification of the entire melt. Fast scanning chip calorimetry revealed different mechanisms of nucleation at low and high supercooling. In comparison to non-nucleated iPP the presence of the β-phase nucleating agent only affects the crystallization kinetics at low supercooling, supporting the idea that ordering at high supercooling is governed by homogeneous nucleation. β-crystals, formed initially on slow cooling, melt below about 420 K on slow heating, followed by formation of few α-crystals on continuation of heating. The mesophase initially formed on fast cooling and aging at ambient temperature, in contrast, recrystallizes directly into α-structure. The results of the present work provide comprehensive information about the condition of formation and the stability of different polymorphs in isotactic polypropylene containing a β-phase nucleating agent.

Understanding the glass-forming ability of active pharmaceutical ingredients for designing supersaturating dosage forms

Kohsaku Kawakami, Toshinori Usui, Mitsunari Hattori

Abstract
Amorphous solid dispersions have great potential for enhancing oral absorption of poorly soluble drugs. Crystallization behavior during storage and after exposure to aqueous media must be examined in detail for designing stable and effective amorphous formulations, and it is significantly affected by the intrinsic properties of an amorphous drug. Many attempts have been made to correlate various thermodynamic parameters of pharmaceutical glasses with their crystallization behavior; however, variations in model drugs that could be used for such investigation has been limited because the amorphous characteristics of drugs possessing a high crystallization tendency are difficult to evaluate. In this study, high-speed differential scanning calorimetry, which could inhibit their crystallization using high cooling rates up to 2000°C/s, was employed for assessing such drugs. The thermodynamic parameters of the glasses, including glass transition temperature (T(\(g\))) and fragility, were obtained to show that their crystallization tendency cannot be explained simply by the parameters, although there have been general thought that fragility may be correlated with crystallization tendency. Also investigated was correlation between the thermodynamic parameters and crystallization tendency upon contact with water, which influences in vivo efficacy of amorphous formulations. T(\(g\)) was correlated well with the crystallization tendency upon contact with water.
A Convenient Route to High-Performance HDPE–CNT Conductive Nanocomposites by Control of Matrix Nucleation

Fangfang Tao, Leïla Bonnaud, Oltea Murariu, Dietmar Auhl, Philippe Dubois, Christian Bailly

Abstract
We show how styrene-ethylene-propylene-styrene (SEPS) triblock copolymer uniquely reduces the electrical percolation threshold after matrix crystallization of conductive nanocomposites based on high viscosity HDPE with low amounts of pristine multiwall carbon nanotubes (CNT). Rheo-dielectric and Flash DSC techniques are used to demonstrate that SEPS interferes with the nucleation ability of CNT on HDPE crystallization in a way that favors contacts between the nanotubes after crystallization as well as it improves CNT dispersion.

Crystallization of a Polyamide 6/Montmorillonite Nanocomposite at Rapid Cooling

Daniela Mileva, Andrea Monami, Dario Cavallo, Giovanni C. Alfonso, Giuseppe Portale, René Androsch

Abstract
The crystallization behavior of a polyamide 6/organo-modified montmorillonite (PA 6/OMMT) nanocomposite has been investigated by scanning chip calorimetry and wide-angle X-ray scattering, with emphasis placed on the evaluation of the effect of supercooling/cooling rate on the crystal/mesophase polymorphism of the PA 6 matrix. Presence of OMMT has negligible effect on the kinetics of formation of α-crystals of PA 6 at low cooling rate while there is observed enhanced nucleation of γ-mesophase on fast cooling. Furthermore, addition of OMMT leads to a distinct increase of the cooling rate required to completely vitrify the amorphous state. The performed experiments demonstrate that the nucleating effect of OMMT in PA 6/OMMT nanocomposites is of particular importance at cooling conditions relevant in polymer processing.

Tailoring the Formation Rate of the Mesophase in Random Propylene-co-1-pentene Copolymers

Ernesto Pérez, José M. Gómez-Elvira, Rosario Benavente, and María L. Cerrada

Abstract
The mesophase structuring has been studied by fast scanning calorimetry in a series of random propylene-co-1-pentene copolymers, up to 7.9 mol % of 1-pentene units. It was found that the formation rate of the mesophase can be easily tailored in a wide range covering 2 orders of magnitude, in such a way that the rates involved in the copolymer with highest comonomer content can be also analyzed by conventional techniques, namely DSC and real-time X-ray diffraction employing synchrotron radiation. The advantage from the standpoint of easiness on the study of mesophase structuring is, therefore, well evident. The penalty to pay is the decrease on the overall degree of order attained in the copolymers.
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<td>59</td>
<td>Procedia Engineering 47 (2012), 140 – 143</td>
<td>Analyzing protein denaturation using Fast Differential Scanning Calorimetry</td>
<td>R. Splinter, A.W. van Herwaarden, E. Iervolino, G. Vanden Poel, D. Istrate P.M. Sarro</td>
<td>This paper investigates the possibility to measure protein denaturation with Fast Differential Scanning Calorimetry (FDSC). Cancer can be diagnosed by measuring protein denaturation in blood plasma using Differential Scanning Calorimetry (DSC). FDSC can reduce diagnosis time from hours to minutes, requiring significantly smaller sample quantities. To show the feasibility of measuring protein denaturation with FDSC, protein denaturation in human hair is measured. We have been able to observe the phenomena of water evaporation and pyrolysis as they were measured in hair by DSC, however, the protein denaturation peaks are largely obscured by the water evaporation and pyrolysis phenomena, as the current set up only allows dry measurements.</td>
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<td>60</td>
<td>Journal Thermal Analysis Calorimetry 110 (2012), 1533-1546</td>
<td>Performance and calibration of the Flash DSC 1, a new, MEMS-based fast scanning calorimeter</td>
<td>G. Vanden Poel, D. Istrate, A. Magnon, V. Mathot</td>
<td>For the new Flash DSC 1, the temperature windows-to-operate—the temperature ranges where the real, achieved scan rate is constant—have been determined for unloaded sensors under various conditions like purge gas and flow rate variations; cooling to -90 °C and heating to 450 °C; scan rates from 1 up to 20,000 s⁻¹ in heating and 15,000 °C s⁻¹ in cooling. Compared to nitrogen, helium purge gas offers better access to low-temperature transitions and enables faster cooling. Drawback is the decreased temperature window-to-operate in heating at the high-temperature side. The temperature calibration protocol according to the recent DIN SPEC 91127 for sample mass and scan rate was found to be useful. The correction factors are maximal -1.4 °C as measured for 1 lg at 1,000 °C s⁻¹ heating. Using liquid crystalline substances it was proved that the Flash DSC 1 has symmetry, meaning that calibration data found in heating also can be applied in cooling.</td>
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<td>61</td>
<td>Polymer 53 (2012), 4770-4777</td>
<td>The rigid amorphous fraction of cold-crystallized polyamide 6</td>
<td>Igor Kolesov and René Androsch</td>
<td>The rigid amorphous fraction (RAF) of polyamide 6 ordered/crystallized on heating initially fully amorphous glassy samples has been analyzed. Variation of the maximum annealing temperature allowed generation of partially ordered samples with different amount, perfection and morphology of mesophase or crystals. In samples with low fraction of mesophase between 0 and 20 %, the RAF increases with increasing mesophase fraction to reach a maximum value of 50 %. Further increase of the fraction and perfection of the ordered phase achieved by annealing at high temperature leads to a decrease of the RAF. The ratio between mobile and rigid amorphous fractions increases with increasing crystallinity, suggesting increasing decoupling of crystals and amorphous phase in samples of high crystallinity, and confirming results obtained earlier on poly(ethylene terephthalate) and isotactic polypropylene. The study contains a comparison of the RAF estimated from calorimetric analysis of the heat-capacity increment and dynamic-mechanical analysis of the area of the loss-factor peak on devitrification the mobile amorphous fraction, and a discussion of the effect of the phase composition of cold-ordered/crystallized PA 6 on the stiffness.</td>
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Ultra-fast calorimetry study of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ crystallization between dielectric layers

J. Orava, A. L. Greer, B. Gholipour, D. W. Hewak, and C. E. Smith

Abstract
Phase changes in chalcogenides such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ can be exploited in non-volatile random-access memory, with fast crystallization crucial for device operation. Ultra-fast differential scanning calorimetry, heating at rates up to $40\,000\,\text{K s}^{-1}$, has been used to study the crystallization of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ with and without sandwich layers of ZnS-SiO$_2$. At heating rates up to $1000\,\text{K s}^{-1}$, the sandwich layers retard crystallization, an effect attributed to crystallization-induced stress. At greater heating rates ($\geq5000\,\text{K s}^{-1}$), and consequently higher crystallization temperatures, the stress is relaxed, and sandwich layers catalyze crystallization. Implications for memory-device performance are discussed.

Quantification of non-isothermal, multi-phase crystallization of isotactic polypropylene: The influence of cooling rate and pressure

M. van Drongelen, T.B. van Erp, G.W.M. Peters

Abstract
The structure of semi-crystalline polymers is strongly influenced by the conditions applied during processing and is of major importance for the final properties of the product. A method is presented to quantify the effect of thermal and pressure history on the isotropic and quiescent crystallization kinetics of four important structures of polypropylene, i.e., the $\alpha$-, $\beta$-, $\gamma$- and mesomorphic phase. The approach is based on nucleation and growth of spherulites during non-isothermal solidification, described by the Schneider rate equations combined with the Komogoroff-Avrami expression for space filling. Using an optimization routine the time-resolved multi-phase structure development is accurately described using crystal phase dependent growth rates and an overall nucleation density, all as function of temperature and pressure. It is shown that the maximum growth rate of the $\alpha$- and $\gamma$-phase increases with applied pressure, while it decreases for the mesomorphic phase. Addition of $\beta$-nucleation agent is interpreted as a secondary nucleation density with a coupled $\beta$-phase growth. This complete crystallization kinetics characterization of isotactic polypropylene allows prediction of the multi-phase structure development for a wide range of quiescent processing conditions.
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<th><strong>Polymer 53 (2012), 4429-4437</strong></th>
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<td><strong>Effect of comonomer partitioning on the kinetics of mesophase formation in random copolymers of propene and higher α-olefins</strong></td>
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<td>Dario Cavallo, Lorenzo Gardella, Giovanni C. Alfonso, Daniela Mileva, René Androsch</td>
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<tr>
<td><strong>Abstract</strong></td>
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<td>The effect of co-unit type on the kinetics of mesophase formation has been investigated by means of chip calorimetry in propene/α-olefin random copolymers, containing co-units which show large differences in their co-crystallization behavior with propene, i.e. 1-butene and 1-hexene. Non-isothermal crystallization experiments indicated that the minimum cooling rate at which mesophase formation is observed is directly related to the kinetic of α-phase crystallization, which is lower for the copolymer with the bulkier 1-hexene co-unit. Isothermal structuring was probed in a wide temperature range, revealing that a double bell-shaped curve is required to describe the temperature dependence of crystallization times of the two polymorphs. The ordering kinetics of the mesophase is the fastest in i-PP homopolymer and decreases with increasing co-monomer bulkiness, analogous to what happens for the monoclinic phase. The results are discussed by considering the effect of co-monomer on the driving force for mesophase formation, also at the light of new WAXD and density evidences, which prove different extents of inclusion of 1-butene and 1-hexene in the ordered phases.</td>
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<th>65</th>
<th><strong>Macromolecules 45 (2012), 5866-5880</strong></th>
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<td><strong>Compositional Analysis of an Impact Polypropylene Copolymer by Fast Scanning DSC and FTIR of TREF-SEC Cross-Fractions</strong></td>
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<td>Sadiqali Cheruthazhekatt, Thijs F. J. Pijpers, Gareth W. Harding, Vincent B. F. Mathot and Harald Pasch</td>
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<tr>
<td><strong>Abstract</strong></td>
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<td>ABSTRACT: For the first time, the complex composition of a two-reactorproduced impact polypropylene copolymer (IPC) has been fully revealed by advanced thermal analysis, using the combination of fast scanning DSC (HPer DSC, flash DSC, and solution DSC) with SEC fractionation subsequent to TREF fractionation. The dual TREF-SEC separation provided fractions of a few micro- or nanograms that were used to correlate the molecular structure of the polymer chains and their thermal properties (melting and crystallization behavior of the different macromolecules under a variety of different conditions). The SEC fractions were collected using the LC transform interface and subjected to FTIR and fast scanning DSC analysis. The SEC curves showed mono-, bi-, and multimodal molar mass distributions. The SEC fractions collected were analyzed by HPer DSC at 50 °C/min by which the thermal properties of the fractions could be established and salient details revealed. The findings were confirmed by structural information that was obtained using FTIR measurements. These results confirmed that even after TREF fractions were obtained they were complex regarding molar mass and chemical composition. By applying HPer DSC at scan rates of 5–200 °C/min and flash DSC at scan rates of 10–1000 °C/s, the metastability of one of the fractions was studied in detail. The high molar mass part of the material appeared to be constituted of both highly isotactic PP and low to medium propylene content ethylene copolymers (EPC). The medium molar mass part consisted of high to medium isotactic PP and of low propylene content EPC. The low molar mass part did not show ethylene crystallinity; only propylene crystallinity of medium to low isotacticity was found. DSC measurements of TREF-SEC crossfractions at high scan rates in p-xylene successfully connected reversely to the slow scan rate in TREF elution, if corrected for recrystallization. All EPC’s show only ethylene-type crystallization. The wealth of information obtainable from these method combinations promises to be extremely useful for a better understanding of the melting and crystallization processes of such complex materials. The ability to run DSC experiments at very high scan rates is an important prerequisite to understanding the melting and crystallization behavior under conditions that are very close to melt processing of these key commodity polymers.</td>
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Morphology of mesophase and crystals of polyamide 6 prepared in a fast scanning chip calorimeter

Daniela Mileva, René Androsch, Evgeny Zhuravlev, Christoph Schick

Abstract
Atomic force microscopy (AFM) has been employed to study the effect of the pathway of nucleation/crystallization on the morphology of the ordered phase of polyamide 6 (PA 6). Samples of PA 6 were crystallized or ordered at different supercooling of the melt, to obtain either α-crystals or γ-mesophase, respectively. For improved control of the nucleation pathway, samples for AFM analysis were for the first time prepared using a fast scanning chip calorimeter (FSC). It has been found that melt-crystallization at low supercooling is connected with the formation of lamellae, while the mesophase formed at high supercooling is of non-lamellar shape. In case of cold-crystallization, the final semicrystalline structure depends on the heating rate; slow heating first leads to formation of mesophase nodules which then reorganize to crystals at elevated temperature, while fast heating suppresses the formation of mesophase and allows direct transformation of supercooled liquid to lamellae. The general approach of using FSC for AFM sample preparation has been confirmed by analysis of the effect of the thermal pathway of ordering/crystallization on the structure of an isotactic polypropylene.

Structure formation of random isotactic copolymers of propylene and 1-hexene or 1-octene at rapid cooling

Daniela Mileva, René Androsch, Dario Cavallo, Giovanni C. Alfonso

Abstract
The effect of variation the cooling rate in a wide range between $10^{-2}$ and 103 K s$^{-1}$ on solidification the relaxed melt of random isotactic copolymers of propylene with low amount of 1-hexene or 1-octene has been studied. Emphasis has been placed on the structure formation at rapid cooling and an evaluation of the conditions required to permit crystallization, mesophase formation, or suppression of any ordering. The presence of low amount of either 1-hexene or 1-octene co-units in the propylene chain decreases drastically the critical cooling rate required for suppression of crystallization from about 150–200 K s$^{-1}$ in the homopolymer to about only 10 K s$^{-1}$ in the copolymers; increasing the cooling rate beyond these limits allowed mesophase formation or even generation of fully amorphous samples. The study of the kinetics of formation of specific structures is completed by a complementary analysis of the X-ray structure, morphology and superstructure of the ordered phase. The hindrance of non-isothermal crystallization and mesophase formation of random copolymers of propylene with 1-hexene or 1-octene is compared with that in propylene–1-butene copolymers; addition of only 2–3 mol% 1-hexene or 1-octene into the propylene chain leads to even larger hindrance of the ordering process than the addition of more than 10 mol% 1-butene.
**Atypical gelation in gelatin solutions probed by ultra-fast calorimetry**

Nathanael Guigo, Nicolas Sbirrazzuoli and Sergey Vyazovkin

**Abstract**

This paper describes the first application of ultrafast scanning calorimetry to the process of gelation in concentrated (40 wt%) aqueous gelatin solutions. It demonstrates that the regular gelation that occurs on cooling can be outrun at sufficiently fast cooling rates (500 K s\(^{-1}\)) so that the solution reaches a metastable supercooled liquid state. Successive heating of the supercooled solution reveals an atypical process of gelation that takes place while continuously raising the temperature. Isoconversional kinetic analysis is applied to treat the atypical gelation process and to compare it with regular gelation on cooling. Although atypical and regular gelation occur on significantly different time scales they appear to have common dynamics.

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**Crystallization and Homogeneous Nucleation Kinetics of Poly(ε-caprolactone) (PCL) with Different Molar Masses**

Andreas Wurm, Evgeny Zhuravlev, Kathrin Eckstein, Dieter Jehnichen, Doris Pospiech, R. Androsch, B. Wunderlich, and Christoph Schick

**Abstract**

The crystallization and nucleation kinetics of poly(ε-caprolactone) (PCL) with molar masses between 1.4 and 6.1 kDa and negligible number of heterogeneous nuclei has been investigated by differential fast scanning calorimetry (DFSC) applying scanning rates up to 100’000 K/s. The samples were synthesized by ring-opening polymerization and chemically characterized by NMR spectroscopy, size exclusion chromatography (SEC), and multiangle laser light scattering (MALLS). For the smallest molar mass the chain length is comparable with the crystal thickness measured with small-angle X-ray scattering (SAXS), and extended chain like crystals may be formed. Because of the molar mass distribution (PDI \(\approx 2\)), these crystals have a significant noncrystalline interface yielding nearly the same crystallinity for all molar masses. The critical cooling rate to obtain amorphous samples is below 1000 K/s and only for the lowest molar mass increased to 2000 K/s. The same trend holds for the about 1 order of magnitude higher critical heating rate to keep the samples amorphous on heating and for the analysis of isothermal nucleation and crystallization kinetics at 202 K. The samples which were shown not to contain heterogeneous nuclei active at a heating rate of >18’000 K/s were used for a study of the nucleation activity of ordered structures formed on annealing at low temperature. The analysis of the change of the thus-produced amorphous polymer samples on annealing from 202 to 272 K for times varying by a factor of more than 10\(^8\) (0.1 ms to 8.3 h) revealed new details about the ordering processes (nucleation, poor crystal formation, crystallization, cold crystallization, and crystal perfection) and the accompanying changes in glass transition of the remaining amorphous phase (formation of rigid amorphous phases, RAF).
**Characterization of supercooled liquid Ge$_2$Sb$_2$Te$_5$ and its crystallization by ultrafast-heating calorimetry**

J. Orava, A. L. Greer, B. Gholipour, D.W. Hewak and C. E. Smith

Abstract
Differential scanning calorimetry (DSC) is widely used to study the stability of amorphous solids, characterizing the kinetics of crystallization close to the glass-transition temperature $T_g$. We apply ultrafast DSC to the phase-change material Ge$_2$Sb$_2$Te$_5$ (GST) and show that if the range of heating rates is extended to more than $10^4$ K s$^{-1}$, the analysis can cover a wider temperature range, up to the point where the crystal growth rate approaches its maximum. The growth rates that can be characterized are some four orders of magnitude higher than in conventional DSC, reaching values relevant for the application of GST as a data-storage medium. The kinetic coefficient for crystal growth has a strongly non-Arrhenius temperature dependence, revealing that supercooled liquid GST has a high fragility. Near $T_g$ there is evidence for decoupling of the crystal-growth kinetics from viscous flow, matching the behaviour for a fragile liquid suggested by studies on oxide and organic systems.

**Temperature calibration and electrical characterization of the differential scanning calorimeter chip UFS1 for the Mettler-Toledo Flash DSC 1**


Abstract
This paper reports on the temperature calibration and electrical characterization of the calorimeter chip UFS1 (internal design XI-400) developed for the new commercially available differential scanning calorimeter (DSC), the Flash DSC 1 of Mettler-Toledo. The chip consists of 2 identical membranes both with a p-type polysilicon microheater in the center of the membrane and a p/n-type polysilicon thermopile for measuring the sample temperature. The temperature calibration of the XI-400 is performed in the temperature range from 208 K to 723 K. An isothermal calibration is first performed to calibrate the heater resistance and the obtained curve is used to calibrate the integrated thermopile. The accuracy of the calibration is then determined by measuring the extrapolated onset temperature ($T_e$) of primary standards. A detailed electrical characterization of the device is also reported. The calibration method implemented and the good temperature reproducibility of the device allow to use devices with uncalibrated heater resistance in the temperature range from 208 K to 723 K with a typical maximum error of ±5 K.
**Thermochimica Acta 522 (2011), 46-52**

**Design, performance and analysis of thermal lag of the UFS1 twin-calorimeter chip for fast scanning calorimetry using the Mettler-Toledo Flash DSC 1**

Vincent Mathot, Marek Pyda, Thijs Pijpers, Geert Vanden Poel, Ernst van de Kerkhof, Sander van Herwaarden, Floor van Herwaarden, Archi Leenaers

**Abstract**
The performance of the Flash DSC 1, a recently introduced, commercial available chip fast scanning calorimeter (FSC) based on MEMS sensor technology, was studied. Topics included calibration; symmetry; repeatability; scan rate control windows of operation. Scan rates up to 20’000 °C/s for empty cell measurements in cooling and heating have been achieved. By combinations of scan rates up to 1000 °C/s various topics in between −95 to 450 °C were studied on polymers including self nucleation; annealing and thermal fractionation; ‘hot’ and ‘cold’ crystallization; amorphization; and cross-over of crystallization behavior with scan rate variation for two polymers. Sample masses around 1 mg and less gave good results with excellent repeatability and acceptable thermal lags. The Flash DSC 1 enables to mimic realistic conditions of practice and to measure (meta)stability and reorganization phenomena of substances and materials, including polymers, metals, pharmaceuticals etc.

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**Procedia Engineering 5 (2010), 464-467**

**Micro-sensors for Analysis Equipment: Research and Innovation**

Sander van Herwaarden

**Abstract**
Xensor Integration has been active in development and production of micro-sensors for customers since more than 2 decades. In that time we have developed products for applications in areas such as space, agriculture, medical and laboratory equipment. In this paper we will briefly discuss some research and development projects we carried out in that time, and then zoom in on an example of such a project, the development of the Flash DSC of Mettler-Toledo. This will give an impression of how unpredictable research and innovation really are. And how projects for space, medical and laboratory applications each have their own specifics.

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**Thermochimica Acta 522 (2011), 36-45**

**The Flash DSC 1, a power compensation twin-type, chip-based fast scanning calorimeter (FSC): First findings on polymers**

Vincent Mathot, Marek Pyda, Thijs Pijpers, Geert Vanden Poel, Ernst van de Kerkhof, Sander van Herwaarden, Floor van Herwaarden, Archi Leenaers

**Abstract**
The performance of the Flash DSC 1, a recently introduced, commercial available chip fast scanning calorimeter (FSC) based on MEMS sensor technology, was studied. Topics included calibration; symmetry; repeatability; scan rate control windows of operation. Scan rates up to 20’000 °C/s for empty cell measurements in cooling and heating have been achieved. By combinations of scan rates up to 1000 °C/s various topics in between −95 to 450 °C were studied on polymers including self nucleation; annealing and thermal fractionation; ‘hot’ and ‘cold’ crystallization; amorphization; and cross-over of crystallization behavior with scan rate variation for two polymers. Sample masses around 1 mg and less gave good results with excellent repeatability and acceptable thermal lags. The Flash DSC 1 enables to mimic realistic conditions of practice and to measure (meta)stability and reorganization phenomena of substances and materials, including polymers, metals, pharmaceuticals etc.
**Structure formation of polyamide 6 from the glassy state by fast scanning chip calorimetry**

_Igor Kolesov, Daniela Mileva, René Androsch, Christoph Schick_

**Abstract**

Fast scanning chip calorimetry has been employed to explore the kinetics of structure formation of polyamide 6 from the glassy state. First, the condition to obtain fully amorphous polyamide 6 has been evaluated. It was found that ordering processes are only permitted on cooling the relaxed melt slower than about 150 K s⁻¹; faster cooling was connected with complete vitrification of the supercooled liquid. Cold-ordering of fully amorphous, non-aged samples on continuous heating only takes place if the heating rate is lower than 500 K s⁻¹. Isothermal cold-ordering experiments of fully amorphous samples have been performed in a wide temperature range between 330 and 470 K, in order to obtain for the first time a complete relationship between half-time of cold-ordering/crystallization and temperature. The study was completed by an initial discussion of the temperature dependence of the mechanism of nucleation and of the effect of the crystal/mesophase polymorphism on the transition kinetics.

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**Precipitation enthalpy during cooling of aluminum alloys obtained from calorimetric reheating experiments**

_Davit Zohrabyan, Benjamin Milkereit, Olaf Kessler, Christoph Schick_

**Abstract**

Precipitation reactions inside aluminum alloys are known to be very important for hardness and yield strength. Premature precipitation during quenching from solution annealing decreases the yield strength after aging. A methodology to determine the amount of precipitates as a function of quench rate (quench sensitivity) for a wide range of aluminum alloys from calorimetric reheating scans is proposed. The method allows determining the critical cooling rate for suppressing precipitation during quenching. Differential fast-scanning calorimetry was applied to cover the cooling rate range needed for high alloyed materials. The critical cooling rate for the quench sensitive EN AW 7049A alloy was determined as 300 K/s. A new methodology, called differential reheating method, was applied for differential fast-scanning calorimetry (DFSC) and differential scanning calorimetry (DSC). The method was quantitatively verified with EN AW 6063 alloy in a DSC due to its low critical cooling rate. The combination of DSC and DFSC extends the available cooling rate range for precipitation studies from mK/s up to some 10,000 K/s.
Fast scanning power compensated differential scanning nano-calorimeter: 1. The device

Zhuravlev, E., Schick, C.

Abstract

Fast scanning calorimetry becomes more and more important because an increasing number of materials are created or used far from thermodynamic equilibrium. Fast scanning, especially on cooling, allows for the in situ investigation of structure formation, which is of particular interest in a wide range of materials like polymers, metals, and pharmaceuticals to name a few. Freestanding silicon nitride membranes are commonly used as low addenda heat capacity fast scanning calorimetric sensors. A differential setup based on commercially available sensors is described. To enhance performance of the device a new asymmetric power compensation scheme was developed. The hardware realization of the scheme and calculation of differential power are presented in the first part of this paper. The fast analog amplifiers allow calorimetric measurements up to 100,000 K/s. The lower limit is defined by the sensitivity of the device and is 1 K/s for sharp melting or crystallization events in metals and ca. 100 K/s for broad transitions in polymers. Another limiting factor is accuracy of sample temperature measurement. A strong dependency of temperature on sample placement on the sensor is observed; even reproducibility is within ±1K. For finite sample thicknesses the commonly observed thermal lag must be considered too. Uncertainty of the temperature measurement based on previous thermopile calibration is in the order of ±10 K. A significant improvement is possible by adding a small particle of a temperature calibration standard, e.g. indium or tin, on top of the sample under investigation. Then uncertainty is about ±3K. The second part of the paper describes sample heat capacity determination and an example to demonstrate the performance of the device.

Verifying the symmetry of ultra-fast scanning calorimeters using liquid crystal secondary temperature standards

Minzhi Chen, Muting Du, Jing Jiang, Dawei Li, Wei Jiang, Evgeny Zhuravlev, Dongshan Zhou, Christoph Schick, Gi Xue

Abstract

The rapid development of fast scanning calorimeters requires new approaches for temperature calibration and symmetry verification at scanning rates above 10 K/s. Liquid crystal materials like 4-cyano-octoxybiphenyl (8OCB), 4-ethyl-4-(4-propyl-cyclohexyl)-biphenyl (BCH-52), 4-(4-pentylcyclohexyl)-benzoic acid-4-propyl-phenyl ester (HP-53), have been recommended by the Gesellschaft für Thermische Analyse e. V. (GEFTA) as secondary standards for symmetry verification of standard DSC instruments. However, fast cooling by chip calorimeter creates metastable states that show, during subsequent heating scans, multiple peaks due to structural reorganization. After structural reorganization by annealing at appropriate temperatures only one peak is observed. We checked the rate dependence of the liquid crystal phase transitions on heating and cooling up to 20,000 K/s. The rate dependence of the nematic to isotropic (NI) transition of 8OCB is continuous between heating and cooling and quite symmetric. So we suggest that 8OCB is qualified as a material for symmetry verification of fast scanning chip calorimeters.
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