

Abstracts Posters

Quiescent and Flow-Induced Crystallization in Polyamide 12 / Cellulose Nanocrystal and PEEK / CNT Nanocomposites

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Both nucleating agents and flow accelerate the crystallization kinetics and alter the ultimate microstructure of semicrystalline polymers. To evaluate the potential synergistic effects of flow and nucleating agents at high supercooling, two polymers, polyamide 12 (PA 12) and polyetheretherkeytone (PEEK), and nanocomposites (PA 12 / CNC) & (PEEK / CNT) of these polymers were investigated. Both neat polymers and nanocomposites were subjected to known amounts of shear work prior to fast scanning calorimetry to determine the nucleation that originates from flow-induced precursors and nanoparticles during isothermal crystallization. In PA 12, the addition of the CNC accelerated crystallization in the heterogeneous nucleation regime ($T > 100$ °C) in the quiescent material. With the addition of shear, the neat system displayed a reduced crystallization peak time with increasing shear history. In the nanocomposite system, the CNCs are an extremely efficient nucleating agent, achieving a saturating limit for nucleation of crystallization, such that shear was only a factor at low supercooling at temperatures greater than 140 °C.

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Delay of re-entanglement kinetics by shear-induced precursors in isotactic polypropylene melt

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Rheological measurements were performed in order to in-situ monitor the re-entanglement kinetics of large amplitude oscillation shear (LAOS) modified isotactic polypropylene (i-PP) melt. The characteristic entanglement recovery times (τ_R) are unexpectedly longer than the corresponding linear viscoelastic relaxation times (τ_d) of the fully entangled melt. The temperature dependence of τ_R and τ_d are the same at temperature range above 210 °C, displaying a typical flow activation energy of about 41.4 kJ/mol. However, a much higher activation energy of around 98.6 kJ/mol, was observed for the entanglement recovery process at temperatures lower than 210 °C. Notwithstanding, the molecular weight dependences of entanglement recovery and linear viscoelastic relaxation followed an equivalent power law (with exponent equal to 3.4). We propose that the re-entanglement process of shear-induced disentanglement in i-PP melt was postponed by the existence of quasi-ordered clusters created by shear at relatively low temperature range and their dissolution is the rate-determining step for the whole recovery, which is consistent with the relaxation model of shear-induced nucleation precursors proposed by Alfonso.[1-3]

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The effect of annealing temperature on the crystalline structure of pre-oriented PLA film

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Firstly, the pre-oriented amorphous PLA films with chi structure were prepared using melt-stretching method. The effect of annealing temperature on their crystalline structure was studied by DSC, XRD and FTIR. It was found that the amorphous phase could transfer to α' crystal directly without the formation of mesophase when annealed at 70°C. The transition process of PLA crystalline structure under different temperature was also given. During annealing at 70-80°C, only α' crystal was found and the formation of crystal was increasing due to the heterogeneous nucleation effect, but the crystal size was increasing less. With the annealing temperature increasing to 90-100°C, some α' crystal would transfer to α crystal but the content of α' crystal was still higher than that of α crystal. The size of α' crystal was increasing obviously. When annealed at 110°C, most of α' crystals were transformed to α crystals directly and the newly formed crystals were α crystal, the growth of α' crystal was less. By further increasing annealing temperature, only α crystal was formed and the size of crystal was increased[1]. With the annealing temperature increasing, the obvious blue-shift of carbonyl absorption band in FTIR spectroscopy occurred since the disorientation of pre-oriented structure weakened the dipole-dipole interaction during crystallization. The variation of the characteristic peak of the infrared group corresponded to the transition of PLA crystal structure during annealing[2]. The pre-oriented chi structure accelerated the crystal formation and showed a significant influence on the transition of PLA crystal structure during annealing.

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Effect of self-assembly of hydrogen bonding compounds on the visco-elastic behavior and crystallization of *i*PP under quiescent conditions and during shear

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Hydrogen bonding organic molecules have attracted significant attention in the recent years due to their role as nucleating agent for polymers such as isotactic polypropylene (*i*PP). In addition, these compounds are known to facilitate an apparent suppression in visco-elastic behavior of the polymer [1]. Unfortunately, a clear understanding on the origin of the viscosity suppression and its effect on *i*PP crystallization under shear is not available. To address these points, in this study we report on the visco-elastic behavior of *i*PP containing an oxalamide based organic molecule using both plate-plate rheology and slit-flow experiments, while monitoring the time-resolved structure development using x-ray analysis[2].

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Unique Daughter Lamellae Evolution Paths Found in Die-drawn Isotactic Polypropylene

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The cross-hatched structure of isotactic polypropylene (iPP) [1] has been proved to be related to the property of the final product, such as fatigue life [2] and wearability [3]. Nowadays, the adjustment of the polypropylene-based products is often achieved by inducing different crystalline forms of polypropylene or adding other polymer materials. Few investigations focus on altering the mechanical property via regulating this cross-hatched structure. In the present work, the authors employed one commercial iPP and processed the material via tensile stretching and die-drawing process. With the help of wide-angle X-ray diffraction technique, the daughter lamellae fractions of the as-deformed samples were obtained. It turned out not only adding nucleating agents could alter the cross-hatched structure but also the deformation method. Adding alpha-nucleating agent could influence the stability of daughter lamellae and consequently the evolution of daughter lamellae exhibited a temperature dependency. As for the beta-nucleated samples, more daughter lamellae were preserved during die-drawing process as a result of the compressional force originating from the die wall.

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Investigating the crystallization behavior of polymer under confinement by fast scanning calorimetry

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Under confinement, unique features of crystallization arise, among which the slowing down and accelerating crystallization on cooling are both reported.^{1,2} Fast scanning calorimetry (FSC) has proved itself as a powerful method to study the crystallization of polymer under confinement, avoiding unwanted crystallization and reorganization by the fast cooling and heating. We studied the isothermal crystallization kinetics of poly(ethylene terephthalate) (PET) thin films. At high undercoolings, two-step crystallization was observed for ultrathin films less than 60 nm, which can be ascribed to the layered distribution of molecular mobility. While at low undercooling or PET capped in sandwich structure, no obvious two-step crystallization was detected. Different to the cases of ultrathin films, syndiotactic polypropylene (sPP) located inside large alumina nanopores indicates a double crystallization phenomenon at slow cooling rates, which is attributed to the fractionated crystallizations initiated by different nucleation mechanisms. Furthermore, we introduced the method of liquid drop enhanced cooling method that after controlling the drop size, proper heating loop cutting, avoiding of Leidenfrost effect, the cooling rate reaches up to 10^5 Kelvin per second, i.e., about 4 orders of magnitude faster than cooling by gas at a 50K difference between the sample and the ambient temperature. This allows for generating a desired metastable state, which can then be investigated by fast heating or even auxiliary morphology technique, such as atomic force microscope (AFM) or X-ray scattering. It significantly extends the application of FSC with other methods in the field of crystallization investment.

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The influence of crystallization on layer adhesion in Fused Deposition Modeling

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Fused Deposition Modeling (FDM), an additive manufacturing technique consisting of layer-wise polymer extrusion, is often faced with the issue of poor layer adhesion. The degree of bonding between adjacent polymer layers is governed by molecular diffusion across the layer-layer interface and will have a major impact on the structural integrity and mechanical strength of the printed part. During printing of semi-crystalline polymers, crystallization is expected to hinder molecular mobility, resulting in a lower degree of bonding if diffusion is halted due to nucleation of crystals. The main parameters influencing both molecular diffusion and crystallization kinetics are temperature and molecular weight. The temperature in a deposited layer is dependent on different printing parameters, such as nozzle temperature, print speed, build plate temperature and the position of the layer above the build plate. Samples, consisting of a wall with a thickness of one layer, encompassing 50 layers, are printed. Using infrared (IR) thermography, the layer temperature is recorded as a function of time. The hence obtained temperature profile is then simulated in a Fast Scanning Chip Calorimetry (FSC) device, which allows for the rapid cooling speeds typically experienced by the extruded polymer. By utilizing both FSC and XRD, the impact of the aforementioned printing parameters on the degree of crystallinity after printing of two polyamide-based polymers with distinct molecular weights is studied. Furthermore, mechanical peel tests are performed to confirm if a higher degree of crystallinity significantly limits layer adhesion. To finally ascertain whether it is crystallization or viscosity that stops interlayer diffusion, the materials' reptation times, obtained from rheological measurements, are compared to their crystallization kinetics.

Successive Self-nucleation and Annealing for the characterization of recycled polyolefin grades

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Recently much effort is being spent to acquire a knowledge on the properties of polyolefins obtained from recycling. Depending on the source, mixtures of polyethylene (PE) and isotactic-polypropylene (i-PP) can be found. In general, the content and the composition of PE and iPP in a recycled grade is a valuable information difficult to obtain due to the complexity of these systems. Thus, molecular fractionation of recycled grades is an obvious approach in order to identify the single component content in a complex blend. However, traditional fractionation methods, like Temperature Rising Elution Fractionation (TREF) and crystallization analysis fractionation (CRYSTAF),¹ are time-consuming, handling toxic solvents, and requiring expensive instruments. A promising route is represented by Successive Self-nucleation and Annealing (SSA) technique,²⁻³ which employs easy and inexpensive DSC methods and, thanks to the inherently fast crystallization behavior of polyolefins, can be carried out at high rates, substantially reducing the analysis time. In this investigation we show the thermal fractionation results that can be achieved by applying the SSA protocol to different blends of recycled polyolefins. The large difference in melting points between the two main components has required the development of a tailor-made self-nucleation protocol, in order to separately study the detailed distribution of crystallizable sequence lengths of the two polymers. Indeed, the recycled samples could be efficiently fractionated, highlighting the presence of iPP and PE chains with different crystallization capability. Furthermore, a better interpretation of the results given by SSA on the recycled blends was achieved by applying the same fractionation protocol to single and blended model materials which mimic the actual recycled materials. Finally a comparison between SSA results and solution-based fractionation techniques has allowed us to establish the limit of applicability of the former technique to these complex systems.

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Crystallization of Multicrystalline PE-*b*-PCL-*b*-PLLA Triblock Terpolymers and PE-*b*-PEO-*b*-PCL-*b*-PLLA Tetrablock Tetrapolymers

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Morphology and crystallization behaviour of complex multi-crystalline polymer systems are studied: PE₂₁^{7.1}-*b*-PCL₁₂^{4.2}-*b*-PLLA₆₇^{23.0} and PE₁₈^{7.1}-*b*-PEO₃₇^{15.1}-*b*-PCL₂₆^{10.4}-*b*-PLLA₁₉^{7.6} with three and four crystallizable blocks (subscripts indicate composition in wt% and superscript M_n values in kg/mol). The blocks are able to crystallize separately and sequentially as proven by DSC and SAXS/WAXS. The three blocks of the terpolymer can crystallize, although PLLA does it by cold crystallization during the heating scan. The four blocks of the tetrapolymer are able to crystallize as well, however, the crystallization of PEO and PCL blocks occurs in the same temperature range. Real time WAXS synchrotron experiments corroborate the crystallization of all blocks and their sequence. Phase segregation in the melt is studied by SAXS to determine how the melt crystallization proceeds: from a single phase, break out or confined crystallization, depending on the segregation strength.

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Polymer crystallization during 3D printing, investigated by Fast Scanning Calorimetry

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One of a task for future applications of plastics is development of 3D printing technology. Particular case of selective laser melting (SLM) offers flexibility in production, but processes involved are very poorly described. Besides complex melting-crystallization-recrystallization during non-linear multi-step temperature treatment, material flow and porosity are the key parameters. Modeling the process of SLM of polymers is of great scientific and application interest.

Reorganization of polymer crystals in micron-sized particles during laser melting is an appropriate task for Fast Scanning Calorimetry (FSC). The heat input, focused on few ten micron-sized particle results in local heating rates up to 100,000 K/s. Followed by relatively slow cooling or annealing above the crystallization temperature, material undergo several successive reheating during melting of the next layers. Possibilities and of FSC for modeling SLM 3D printing of polymers are discussed and first results demonstrated.

The fingerprints of homogeneous nucleation and crystallization in Polyamid-66 as studied by combined InfraRed (IR) Spectroscopy and Fast Scanning Chip Calorimetry

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Employing a novel calorimetry chip accomplished with an InfraRed (IR) transparent SiN membrane enables one to carry out IR spectroscopic measurements and Fast Scanning Chip Calorimetry (FSC) on the identical sample of poly(amide-66) having an amount of material as small as ~ 100 ng. By that it is possible to achieve cooling rates as fast as 5000 K/s and to quench the sample in the fully amorphous state. Annealing the sample for a certain time τ_i at a given temperature T allows to determine the onset of nucleation and crystal growth based on FSC and to unravel the molecular interactions from the analysis of the IR – spectra. A wealth of findings is observed, such as different molecular moieties of poly(amide-66) show a specific performance in the course of homogeneous nucleation and crystal growth or interactions leading to homogeneous nucleation are hierarchically ordered. Far reaching interactions (H-bonding) are earlier involved than short-range steric ones as exemplified for the $\sigma(\text{CH}_2)$ scissors vibration.

Interfacial Energetic Curvature Properties and their Role for the Nucleation in Polymer Melts

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The interfacial tension between melt and crystal phase is usually viewed to be the most important thermodynamic quantity of the interface triggering nucleation as the first step in crystallization. Since nucleation is a nanoscopic scale process, it is not surprising, that even thermodynamic equilibrium properties have to be generalized in a proper way. The basic idea one finds already in the work of Gibbs [1], cited also by Tolman [2], who described the relation between the interfacial tension of a flat and of a curved interface with a parameter nowadays called the Tolman length.

The disregarded basic idea of Gibbs can be worked out in a natural way for the extension of thermodynamics including the two basic curvature properties, i.e. mean curvature and Gaussian curvature [3] and using the required geometric concepts as introduced by Steiner [4]. The two corresponding additional energetic properties are the edge force and the item energy. The first one can be negative at temperatures above the thermodynamic equilibrium melting point.

In the generalized Young-Laplace equation an additional term proportional to both Gaussian curvature and edge force shows up. The corresponding extension of the Becker and Döring nucleation theory leads to stable clusters in the melt, for temperatures even above the melting point. At a characteristic undercooling (dependent on the edge force) one obtains spontaneous homogeneous nucleation of these clusters. Also for nucleating agents, the corresponding two-component interfacial energetic curvature properties have to be taken into account.

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Quantification and modeling of multi-phase crystallization of polyamide 12

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The crystallization of Polyamide 12 (PA12) has been investigated using DSC, Flash-DSC and a new experimental setup that allows for in-situ synchrotron Wide Angle X-ray Diffraction (WAXD) combined Flash-DSC measurements. The experimental results are used to parameterize and validate a new numerical model to quantify the quiescent crystallization kinetics, of the three important crystal structures of PA12, i.e. the alpha', gamma and mesomorphic phase. The experimental approach is based on both, isothermal and well defined non-isothermal procedures, The results are described by extended, multi-phase Schneider rate equations, which takes into account the transitions between different phase, and the Kolmogorov-Avrami expression for the space filling. The experimental overall crystallization rate, expressed in terms of the crystallization half-time, as well as the phase composition, are well captured by the model over a wide range of temperatures, i.e. between the glass transition and the melting temperature. It is shown that at temperature below and above 100°C different nucleation mechanisms are dominant causing the bimodal dependence of the crystallization rate.

Crystallization and Microstructure of Side-chain-substituted Poly(lactic acid)s

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Recently, the side-chain-substituted poly(lactic acid)s (SPLAs) have attracted much attention as novel bio-based plastics to overcome weakness of poly(L-lactic acid) (PLLA). However, their possibility as crystalline plastics still remains unexplored. In this study, we focused on crystalline SPLAs with isopropyl and *sec*-butyl side chains [P(L-iPr) & P(L-s-Bu)]. Crystallization, microstructure, and thermal properties of these SPLAs were systematically investigated and compared with PLLA [1-3].

P(L-iPr) and P(L-s-Bu) ($M_n = 60\text{--}70$ kg/mol) were synthesized by ring-opening polymerization of cyclic dimers of corresponding L- α -hydroxy acids obtained by diazotization of L- α -amino acids [1-4]. It was found that WAXD crystallinity of P(L-iPr) (60%) was higher than that of P(L-s-Bu) (30%). Solvent and thermal annealing gave crystal polymorphs of P(L-iPr) (α - & β -forms). On the contrary, no polymorphism was seen in P(L-s-Bu) irrespective of annealing conditions. Maximum spherulite growth rates of SPLAs were in the order of P(L-iPr) (>4.2 $\mu\text{m/s}$) $>$ PLLA (0.17 $\mu\text{m/s}$) \approx P(L-s-Bu) (0.16 $\mu\text{m/s}$). Observed maximum and equilibrium melting points ($T_{m,\text{max}}$ & T_m°) of SPLAs were in the order of P(L-iPr) (222/240 $^\circ\text{C}$) $>$ P(L-s-Bu) (193/n.d. $^\circ\text{C}$) $>$ PLLA (177/200 $^\circ\text{C}$). Thus, side-chain substituents have a great effect on structure and properties of SPLAs. Since both P(L-iPr) and P(L-s-Bu) have better properties compared to PLLA, these SPLAs are expected as excellent bio-based crystalline plastics.

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Band spacing in poly(3-hydroxybutyrate) and its blends with poly (propylene carbonate): dependence on thermal processing

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The band spherulites grown in neat poly(3-hydroxybutyrate) (PHB) and its blends with poly (propylene carbonate) (PPC) were observed by polarized optical microscopy (POM). For the spherulites in neat PHB, it is evident that the band spacing increases first and then decreases with melting times. When the melting time is short, the band spacing increases continuously, which should be attributed to increasing mobility of polymer chains or decreasing viscosity of the melt. As the melting time is prolonged, evident thermal degradation of PHB occurs and results in a great deal of non-crystallizable fractions, which is similar with addition of miscible amorphous polymers in the melt, and the band spacing decreases accordingly. The thermal degradation of PHB cannot, however, be detected by thermogravimetric analyzer, due to less volatile productions. An evident decrease of molecular weight of PHB can be measured by gel permeation chromatography, indicating occurrence of serious degradation. The decrease of crystallization and melting temperature revealed by differential scanning calorimetry (DSC) also prove the thermal degradation. For spherulites in PHB/PPC blends, however, the changing trend of band spacing differs from that in neat PHB. The band spacing increases continuously when melting time is within 15 min. The crystallization and melting behaviors are not influenced greatly by prolonging melting times in PHB/PPC blends. The molecular weight of PHB in PHB/PPC blends changes slightly with prolonging melting time. It is conjectured that the presence of PPC may prohibit the degradation of PHB to some extent, and the mechanism is unclear now. The present results may shed some light on application of PHB and understanding the formation mechanism of banded polymer spherulites

The efficiency of nucleating agents for thermoplastic polyurethanes strongly depends on cooling rates

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When a nucleating agent (NA) is added to a semi-crystalline commercial thermoplastic polyurethane (TPU), the nucleation density and crystallization temperature can be greatly increased, when slow to moderate cooling rates from the melt are used. Reference [1] reports that at high cooling rates, comparable to those used in injection molding, TPU self-nuclei become inactive. In the present study, we have added different NAs to a commercial TPU and we have studied the crystallization, self-nucleation (SN) and morphology of the materials employing DSC, PLOM and SAXS techniques, as a function of cooling rates. When the cooling rate is higher than 200 °C/min, the nucleating efficiency of the NA is dramatically reduced.

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Study of the miscibility of Linear PE with Low density PE and Poly(ethylene-co-1-hexene) through single crystals melting point analysis

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In this work we analyze the miscibility of LPE with branched PEs of different molecular architecture (LDPE and LLDPE types). The method used is the analysis of the melting point depression of LPE single crystals embedded in a matrix of branched PE. The LLDPE samples are poly(ethylene-co-1-hexene) copolymers with narrow molar mass distributions and homogeneous comonomer distribution. The materials, with a range of comonomer content from 0 to 10 % molar, have been obtained by polymerization with single-site catalysts [1]. Details about LDPE samples can be found in reference [2].

From the results obtained by Martínez-Salazar et al. for LPE/LDPE systems, Zhao and Choi [3] discussed that the critical average branch content of LDPE for miscibility is only of about 2 branches per 100 backbone carbons. However, in the case of the LPE/LLDPE systems the critical average branch content of LLDPE is about 6 branches per 100 backbone carbons. This late experimental results are in agreement with those reported by Nicholson et. al by Neutron Scattering [4], emphasizing, at the same time, the important role that the molecular architecture plays on the miscibility of PE family.

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Crystallization and miscibility of solid polymer electrolytes

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In the field of polymer electrolytes, it is known that the crystallinity restricts the ionic conductivity. In this work the effect of lithium salt (LiTFSI) and poly (lithium 1-[3 (methacryloyloxy) propylsulfonyl]-1-(trifluoromethylsulfonyl) imide) (PTFSILi) on PEO crystallization was studied. First, the effect of LiTFSI on the crystallization of aliphatic polyethers with different number of methylene units (between 2 and 12) in the polymer repeating units was studied. The crystallization temperature (T_c) and overall crystallization rate ($1/\tau_{50\%}$) increases with the number of methylene units and decreases with the amount of salt, furthermore, the salt has a diluent effect on the polyethers, this effect was studied using the Flory-Huggins theory for polymer-diluent mixtures, and it was possible to calculate the interaction energy density parameter (B). We show that this value must be small to increase the ionic conductivity.

Additionally, PEO/PTFSILi blends were prepared and the effect PEO molecular weight was studied. The blends were found to be miscible according to the thermal transitions behavior and the predictions of the Nishi-Wang theory. The PTFSILi was obtained by RAFT polymerization and inverse emulsion polymerization with different molecular. The melting temperature (T_m) of PEO decreases with the amount of PTFSILi, also, the glass transition temperature (T_g) increases in the blends with the content of PTFSILi. The spherulitic growth rate of the PEO component in the blends decreases with the content of PTFSILi and this effect is more noticeable with PTFSILi of high molecular weight. On the other hand, the nucleation density was greatly enhanced with the incorporation of PTFSILi in the blends. As a result, the overall crystallization rate ($1/\tau_{50\%}$), which includes both nucleation and growth, experienced a small increase as PTFSILi content increased in the blends. Finally, the values of ionic conductivity obtained for the PEO/PTFSILi blends were in the order of 10^{-4} S cm⁻¹ at 70 °C.

Determination of the critical secondary nuclei size of polymer lamellar crystals

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Nucleation is a fundamental step of polymer crystallization and the mechanism is not fully understood yet [1]. The nucleation rate is predominantly affected by the energy barrier to form the critical nuclei. Determination of the critical nuclei size is a key to understanding the nucleation mechanism, though it has been a great challenge both from experimental and theoretical aspects. In this work, we propose a method to determine the size of the critical secondary nuclei of polymer lamellar crystals. For the secondary nucleation, the slope of the log-log plot of the spherulite radial grow rate versus the content of crystallizable units in the random copolymers gives the number of units in the critical secondary nuclei. This method is based on the stochastic feature of nucleation of random copolymers during crystallization and is independent of the detailed nucleation pathway. Our results on the poly(butylene succinate-co-butylene methylsuccinate) random copolymers show that a critical secondary nucleus consists of 15 to 27 butylene succinate units, corresponding to 6 to 9 chain stems when isothermally crystallized from quiescent melt at the temperatures ranging from 70 to 95 °C. The results contradict the classical Lauritzen-Hoffman theory, which predicted that the critical secondary nucleus should be a single chain stem. Our method can be generally applied to the lamellar crystals of other flexible polymers and would be beneficial to deepen our understanding of the nucleation mechanism.

Keywords: Secondary nucleation; critical nuclei size; polymer lamellar crystals; microscopic kinetics model

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Evaluation of a novel soluble α -nucleating agent for polypropylene

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Soluble α -nucleating agents or clarifiers are widely used in order to improve the mechanical as well as optical performance of isotactic polypropylene (iPP) homo- and copolymers. Sorbitols and trisamides are reoccurring structural motives within this class of substances. Among them, the most prominent example is 1,3:2,4-Bis(3,4-dimethylbenzylidene)sorbitol (DMDBS), commercially available from numerous suppliers but best known under the trade name Millad 3988 of Milliken Inc., USA.

A substance from a class of novel nucleating agents based on symmetrical dibenzoyl hydrazides has been recently commercialized under the trade name TMC-300 by Shanxi Oriental Faith Tech Co. Ltd, China. While marketed as nucleating agent for PLA and polyamides, it has also been tested in iPP [1,2].

We report a comprehensive evaluation of TMC-300 as α -nucleating agent for two iPP resins, a homopolymer and a C3C4-copolymer. The concentration dependency of thermal, rheological, mechanical and optical properties was investigated and compared to DMDBS. It could be proven that TMC-300 acts as a nucleating agent for iPP, however with a performance being inferior to the benchmark.

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Oxo-Biodegradability of High-Density Polyolefin Films containing Different Amounts of Pro-Oxidants: Crystallinity Approach

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The issue of degradable polyolefins have a long history and dates back to 1970s. One of the subclasses of these types of polyolefins is oxo-biodegradable polyolefins.[1] The instability of polyolefins is not harsh enough to degrade the polymer in a short period of time. Polyolefins containing pro-oxidants/pro-degradants additives are one of the solutions. These additives are basically transitioned metal stearate complexes which can accelerate photo and/or thermal oxidation process.[2, 3] In the present work, four different amounts of Addiflex additive (0%w/w, 1%w/w, 3%w/w, and 5%w/w) were added to High-Density Polyethylene (HDPE) and extruded with a twin screw extruder and converted into film with a film blowing process. The films were exposed to UVC light ($\lambda=254$ nm) in a UV chamber for 1008 hours. Changes in crystallinity of the samples were monitored by Differential Scanning Calorimetry (DSC). Results showed crystallinities of the samples with different amounts of the Addiflex additive increased considerably with respect to the neat sample; but compared to the sample with 3%w/w of the additive, the crystallinity of the sample with 1%w/w Addiflex additive increased more. This observation can be attributed to possible crosslinking and radical reactions occurring due to overdosing of the additive which might act as a retarding agent in this period of time.

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Nano-oriented crystals of fluorocarbon polymer formed

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“Nano-oriented crystals (NOC)” of fluoroplastic was formed by the melt-elongational crystallization. NOC shows the morphology which nano-crystals (NC) are closely arranged mainly along the machine direction [1-3].

We used vinylidene fluoride - tetrafluoroethylene copolymer; P(VDF-TFE), as a kind of fluoroplastics. It is well known that P(VDF-TFE) is a ferroelectric polymer. In general, we have to give orientation and poling to a sheet in order to indicate ferroelectricity. Here β form is the ferroelectric phase [4,5].

NOC of P(VDF-TFE) crystallized under weak elongational flow and directly did into β form sheet with high crystallinity from the melt. We verified NOC formation by means of optical microscope and small/wide angle X-ray scatterings.

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Crystallization and self-nucleation of conjugated polymers

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It is well known that the specific conditions under which polymer crystallization occurs dictate the resulting semicrystalline morphology and, therefore, the properties of the solidified material. Even seemingly small differences in degree of crystallinity, lamellar orientation, or number of tie chains between crystallites can result in significant changes in mechanical, optical, or diffusive properties [1-2]. For conjugated polymers, the details of semicrystalline morphology (degree of crystallinity, crystalline perfection, and tie chains) have a tremendous impact on charge transport properties [3]. However, the interplay between chain structure, crystallization conditions, and structure development remains elusive because conjugated polymers typically solidify under ill-defined flow and thermal conditions while a solvent evaporates relatively quickly (for example, during spin coating).

Here, we explore the crystallization behavior of poly-3-hexylthiophene of various molecular weights under well-defined conditions. The results suggest that memory can play an important role in the way crystallization proceeds. Also, we show that self-nucleation can effectively be used to change the conditions under which crystallization occurs, rendering it a potential strategy to manipulate the resulting semicrystalline morphology.

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Segmental Dynamics and Crystallization of poly(L-lactic acid) Oligomer Confined in Alumina Nanopores

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In recent years, the unique glass transition and crystallization phenomena of polymers under 2-dimensional nanoconfinement have attracted increasing attentions[1,2]. We investigated the segmental dynamics and crystallization behavior of poly(L-lactic acid) (PLLA) oligomer confined in anodic alumina oxide templates (AAO) by calorimetry. PLLA oligomer located inside pristine AAO nanopores reveals the suppressed crystallization and heterogeneous segmental dynamics, which induces a broad cold-crystallization peak at higher temperatures. After the surface modification of nanopores by fluoroalkyl silane, the segmental dynamics and cold-crystallization temperature of PLLA nanorods are recovered to the bulk state. Besides, due to the isochoric confining geometry of AAO nanopores, the segmental dynamics and cold-crystallization of PLLA oligomer displayed a pronounced cooling rate effect. For PLLA nanorods hyperquenched in liquid N₂, the polymer chains are peeled off from pore wall by thermal stress, one single glass transition is detected, and unexpected acceleration of cold-crystallization happens, which could be ascribed to the surface-induced nucleation.

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Differences between isotropic and self-nucleated PCL melts

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In this work, the phenomenon of melt memory in polymer crystallization is explored. Depending on the temperature of annealing, the melt can be either isotropic or self-nucleated. Melt memory effects on polymer crystallization have been reported in the literature, although their nature is not completely understood. We have employed dielectric and rheological measurements in order to study the isotropic and self-nucleated melt state of polycaprolactone. The results obtained reveal a reduction of the permittivity for the self-nucleated melt in comparison with the isotropic melt, which means that the mobility of the molecular dipoles is restricted in the self-nucleated melt state. The results obtained by dielectric permittivity are well correlated with significant changes obtained by rheological and DSC measurements, see references 1 and 2.

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Structure formation in nanolayered comb-like and linear precision polymers – A comparative study

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Comb-like polymers with rigid backbones and flexible alkyl side chains form an interesting class of functional materials which find potential applications in organic semi-conductors, electrolyte fuel cells and light weight composites. Precision polyethylenes, synthesized by ADMET polymerization having precise control over placement of functional groups placed regularly along a linear polyethylene chain, are another interesting class of nanolayered materials. A major difference between both polymer classes is, however, that chain connectivity leads to different types of constraints. Here we present results of a comparative study using X-ray scattering and calorimetry highlighting similarities and differences in structure formation in comb-like alkoxyated polyesters and precision polyethylenes having a diaminopyridine ring placed regularly along the chain. In both cases the ring-like sub-units and the alkyl sequences self-assemble in the form of layers on the length scale of 2-3 nm. Of special interest is the competition of the individual packing tendencies of rings and methylene sub-units driving polymorphic behavior which is a commonly encountered phenomenon in such nanolayered systems. The influence of shear fields and interfaces on the structure formation will be also briefly discussed.

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Surface structure analysis of new adhesive using side chain crystalline polymer

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The adhesives are used for temporary fixation of products between two different materials. The properties of the adhesives are dependent on surface and bulk morphology. We focused on temperature-sensitive adhesives (NITTA corp.). This adhesive is non-tacky in the room temperature, on the other hands, it becomes tacky and sticky above the softening temperature. The reason might be melting phenomenon of melting of crystallizable side chain [1]

In this study, we focused on double-sided adhesive tapes due to differences in physical properties such as adhesion strength and peeling performance between each side. Therefore, we observed surface and bulk morphology of both surfaces exposed at the film (subsequent to the front-side) and protected by the film (subsequent to the back-side). We observed the micron scaled hard particles only on front-side with AFM measurements and no structure on back-side. After heat-treatment above 100°C, the hard particles grow on both sides. These results suggest that the hard particles were hidden in the back-side of adhesives, then we focused on the evaporating process during making double-sided adhesive films. On thinner adhesive films, we could observed the hard particles on both side. Furthermore, we carried out AFM measurements on adhesives on various evaporating process is significant on surface properties.

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The microstructure of amphiphilic, self-organized fungal protein films at the air/water interface

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Small amphiphilic fungal proteins named Hydrophobins play various roles during the fungal life-cycle all attributed to their surface activity and propensity for self-assembly. They are divided into two classes based on the morphology and solubility of their primary aggregates: water-insoluble fibrils for class I and closed membranes for class II.^[1] We investigated the self-assembled structures of class I SC3 and class II HFB2 transferred to mica from the air/water interface by the Langmuir-Schaefer (LS) technique using atomic force microscopy (AFM). The main focus was the influence of areal constraint and multiple compressions and expansions on the morphology of the protein films. SC3 shows a more homogenous covering of the mica surface with fibrillary structures. Multiple compressions to a surface pressure of 13 mN/m lead to a shortening of the fibrils. HFBII exhibits multi-layered structures of varying thickness at higher surface pressures. Multiple compressions lead to a variety of large multilayer aggregates, but overall homogenize the films in both cases. Surprisingly both proteins showed similar dendritic structures at pressures of 13 mN/m and above, although the primary structures they assemble into are different. This may be caused by capillary forces upon drying but implies great control over the morphology. Additionally interactions with liposomes containing spin-labeled fatty acids in solution were investigated using dynamic light scattering (DLS) and electron paramagnetic resonance (EPR) spectroscopy. Their presence at the bulk/liposome interface reveals strong interactions with the lipid bilayer for both classes and concentration-dependent changes on the rotational mobility and direct environment on the radical probe.

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SAXS analysis of temperature responsive waterborne block copolymers

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Waterborne ABA block copolymers containing crystalline or hard A block and soft middle B block, were synthesized via two-step reversible addition fragmentation chain transfer (RAFT) polymerization, using S,S-dibenzyl trithiocarbonate (DBTTC) bifunctional RAFT agent [1]. Phase separation morphological properties were studied by means of AFM and TEM microscopic techniques after direct film formation from the dispersion at room temperature and after different annealing techniques. Phase separation confined in the particles was shown in the films dried at room temperature, while particle coalescence and higher ordering was obtained upon film annealing above the melting temperature (T_m) of the crystalline domains or the glass transition temperature (T_g) of the hard domains.

In order to analyze the morphology under different temperature conditions, SAXS was carried out at (i) 30°C on the films dried at room temperature, (ii) above the T_m or T_g of the crystalline or hard domains, and at (iii) 30°C again after the annealing at high temperature. The influence of the different block lengths and that of the film formation temperature on the final morphology was analysed.

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Separate T_g and T_m control in isodimorphic poly[(butylene succinate)-*ran*- ϵ -caprolactone] copolyesters

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High and Low molecular weight poly[(butylene succinate)-*ran*- ϵ -caprolactone] copolyesters (PBS-*ran*-PCL) were synthesized in a wide composition range and detailed comparison is presented. DSC and WAXS showed that these copolyesters are isodimorphic and display double crystallinity at the pseudo-eutectic region. An increase in molecular weight of the copolyester does not influence T_m and T_c , as their values are determined by the randomness of the comonomer distribution. However, crystallinity values are higher for lower M_w copolymers because of their faster crystallization rate. Copolymers with higher M_w exhibited higher T_g values as expected for random copolymers that are characterized by a single phase in the amorphous regions. A remarkable separate T_g and T_m control can be achieved by varying composition and molecular weights in these isodimorphic copolymers that is useful to tailor their properties.

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Effect of entanglements on the semicrystalline morphology as studied by solid-state NMR

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The structure of melt-crystallized semicrystalline polymers strongly depends on the interplay of the different dynamics in the crystalline and amorphous phases as well as on the topological restrictions of entanglements in the melt [1]. The morphology of poly(ϵ -caprolactone) (PCL) has, in agreement with classical crystallization theories, a well-defined thickness of the crystalline lamellae, while the thickness of the amorphous phase is controlled by entanglements [2].

The addition of short chains from the same species prior to crystallization reduces the entanglement density in the melt and allows to study the influence on the structure formation, while all other parameters are kept constant.

The studied PCL samples vary in molecular weight and are diluted with different mass contents of their oligomer. The morphology of diluted PCL samples, crystallized at several temperatures, are characterized by proton time-domain NMR technique and small-angle X-ray scattering. Proton static double-quantum and carbon-13 MAS NMR yield information about the dynamics in the entangled melt and the amorphous phase. Complementarily, polarization microscopy is used to quantify the lamellar growth rate.

Further similar investigations on poly(ethylene oxide) (PEO) address the relationship of entanglement effects in polymers that exhibit intracrystalline dynamics, i.e. chain diffusion arising from a jump-like motion within the crystalline lamellae [3].

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Lamellar thickening of POM - as consequence of intermediate crystalline dynamics

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Depending on the presence or absence of an α_c -relaxation it is possible to distinguish between crystal-mobile and crystal-fixed semi-crystalline polymers. Only crystal-mobile polymers own a certain chain mobility in the crystalline phase [1]. A fast α_c -mobility as in PEO causes a thickening of the crystalline lamellae on the timescale of the crystallization process, leading to a high crystallinity and playing a crucial role for morphology. The lamellae show a larger crystal thickness and higher thermal stability than crystal-fixed polymers [2]. The timescale of the α_c -relaxation can be determined with NMR. For PEO α_c -relaxation takes place on the timescale of μs [3]. With comparatively slow SAXS or DSC measurements we observe the final result of a crystallization process influenced by α_c -relaxation. A change of the polymer system to Polyoxymethylene (POM), a polymer with intermediate crystalline dynamics, enables us to follow changes caused in α_c -relaxation in situ. Using NMR, SAXS and Flash-/DSC we try to fill the gap between polymers without intra-crystalline dynamics like PCL and polymers with fast intra-crystalline dynamics as the above mentioned PEO. NMR-measurements verify a slow α_c -relaxation on the timescale of ms with an activation energy of around 100kJ/mol. Time-dependent SAXS-measurements during isothermal crystallization allows us a clear determination/separation between the primary crystallization process and the lamellar thickening caused by α_c -relaxation. The morphology strongly depends on the crystallization time t_c . With increasing t_c the amorphous phase seems to be minimized.

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Crystalline elastomers based on copolymers of syndiotactic polypropylene with branched comonomers

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We report a study of the structure and mechanical properties of copolymers of syndiotactic polypropylene (sPP) with different comonomers, as ethylene, butene, hexene, octene etc., up to long branched α -olefins. All these copolymers show elastomeric properties even though they present non negligible level of crystallinity at low comonomeric units concentration. The relationships between structure, crystal morphology, stress-induced phase transformations and mechanical properties have been clarified. In samples with low comonomer content the elastic properties are associated with a reversible polymorphic transition between different polymorphic forms of sPP characterized by chains in *trans*-planar and helical conformations that occurs upon stretching and releasing the tension. These phase transformations provide an enthalpic contribution to the elasticity. Samples with higher comonomer concentrations show very low crystallinity and a typical thermoplastic elastomeric behavior with a classic entropic elasticity. The study of the crystal morphology shows the presence of small bundles of rod-like lamellar crystals in all copolymers whose size decreases with increasing content and size of comonomeric units. The small needle-like crystals act as knots of an elastomeric lattice, accounting for the classic entropic elastic properties. Young modulus and strength of these materials can be easily tuned by suitable modification of type and concentration of the comonomeric unit to be copolymerized with propylene that, indeed, affect the degree of crystallinity and the level of entropic and enthalpic contributions to the elasticity. These copolymers represent a new class of elastomeric materials, defined “crystalline elastomers” where the crystallinity plays a fundamental role.

Interface Controlled Thermodynamics of Prefreezing – An Experimental Validation of the Phenomenological Theory

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Heterogeneous nucleation and prefreezing are two possible mechanisms by which a solid surface can induce crystallization of liquids. In contrast to heterogeneous nucleation, first-order prefreezing is an equilibrium phenomenon that refers to the reversible and abrupt formation of a crystalline layer of thickness l_{min} at an interface to a solid surface at the temperature T_{max} well above the bulk melting temperature T_m [1, 2]. Thickness of the prefrozen layer (T) diverges upon further cooling to bulk T_m [1]. Most recently developed phenomenological theory of prefreezing [3] predicts T_{max} to be a function of the difference of interfacial free energies $\Delta\gamma \triangleq \gamma_{sub,melt} - (\gamma_{sub,cry} + \gamma_{cry,melt})$ and $\gamma_{sub,melt}$, whereas l_{eq} and l_{min} are determined by $\gamma_{sub,melt}$ and $\Delta\gamma/\gamma_{sub,melt}$ respectively. Here, we provide an experimental test of the theory by extending our investigations of prefreezing of poly(ϵ -caprolactone) (PCL) on graphite to a MoS₂ substrate. Using in-situ AFM measurements at elevated temperatures, we determine equilibrium properties of the prefrozen PCL layer on MoS₂. These properties include the temperature range of prefreezing, prefrozen layer thickness $l_{eq}(T)$ above the bulk T_m , and discontinuous jump in thickness l_{min} at T_{max} . In comparison with PCL-HOPG, we find a clear decrease in (T) and l_{min} but T_{max} remains nearly unaffected. We analyze our experimental results with the phenomenological theory [3] and estimate the material parameters at the solid interface. A comparison of the material parameters for prefrozen PCL on MoS₂ and HOPG confirms that above mentioned experimental observations are in good agreement with the predictions of the phenomenological theory.

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Cooling rate influence on PVDF based diblock and triblock copolymers polymorphic behavior

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Poly(vinylidene Fluoride) PVDF is a polymorphic polymer and displays different phases when it crystallizes. The most interesting of them are the ferroelectric phases [1]. The ferroelectric phases are β , γ , and δ , while the α -phase is paraelectric [1].

In this work, PE-*b*-PVDF and the PE-*b*-PS-*b*-PVDF copolymers with different compositions are studied [2]. Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), Polarized Light Optical Microscopy (PLOM), Wide Angle X-ray Scattering (WAXS) and Small Angle X-ray Scattering (SAXS) techniques were used to analyse how polymorphism affects the properties of the materials.

When the cooling rate is high (60°C/min), the paraelectric phase is the most abundant one, but on the other hand if the cooling rate is reduced to 1°C/min the ferroelectric phases are enhanced. These materials offer a wide range of applications in energy generation and storage.

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Thermodynamic Principles of the First-Order Prefreezing

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Crystallization of liquids on a solid surface can be initiated by either heterogeneous nucleation or prefreezing. The latter phenomenon is the crystalline layer formation at an interface to a solid substrate at temperatures higher than that of a bulk crystal [1]. Most recently, it was ascertained that prefreezing is a first-order transition, since the formation of the crystalline phase is abrupt and reversible [2].

We introduce a phenomenological theory of prefreezing and analyze such equilibrium properties as the temperature dependent thickness of the prefrozen layer, the maximum melting temperature T_{max} , and the mesoscopic jump of thickness during melting or crystallization l_{min} [3]. The theory provides a clear thermodynamic explanation of the abrupt formation of a crystalline layer, i.e., the first-order nature of prefreezing as a result of the interplay of the interfacial energies $\gamma_{sub,cry}$, $\gamma_{cry,melt}$, and $\gamma_{sub,melt}$. The corresponding transition temperature T_{max} was found to depend on all three interfacial free energies and bulk parameters, whilst the normalized jump of thickness is a function of the interfacial free energies only. We show that the difference of the interfacial energies $\Delta\gamma = \gamma_{sub,melt} - (\gamma_{sub,cry} + \gamma_{cry,melt})$ acts as a driving force for prefreezing, as T_{max} tends to increase with increasing $\Delta\gamma$. The analytical outcomes are congruent with recent experimental results for poly(ϵ -caprolactone) crystallized on graphite via prefreezing.

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Quantitative SAXS analysis of semi-crystalline morphology

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Semi-crystalline polymers crystallized from the melt typically form a nanoscopic two-phase structure of lamellar crystals separated by amorphous layers. This structure, namely the thicknesses of the crystalline and amorphous layers as well as the respective thickness distributions depend strongly on the specific polymer and crystallization temperature. In order to analyze the impact of these parameters on the semi-crystalline morphology accurate determination of all structural parameters including the widths of the thickness distributions is necessary

We present a quantitative analysis of Small Angle X-ray Scattering data, which fulfills this requirement. Based on the description of the semi-crystalline structure in terms of lamellar stacks, the one-dimensional interface distribution function is calculated directly from scattering data. Furthermore, based on the paracrystalline model the interface distribution function is modelled by using Gaussian distributions to represent the distribution of lamellar and amorphous thicknesses, respectively. This modelling is done in reciprocal space in order to avoid truncating the interface distribution function after a few terms. A criterion for the limit of applicability of the model is discussed. For easy application of this analysis, a graphical computer program is presented.

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Influence of Aging on the Nucleation of Glassy Isotactic Polybutene-1 during Cold Crystallization

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Aging of glassy isotactic polybutene-1 (iPB-1) below the glass transition temperature (T_g) leads to easier formation of crystal nuclei and then remarkably accelerates the subsequent isothermal crystallization. The formation of crystal nuclei from the aging temperature to the crystallization temperature has been probed by fast scanning chip calorimetry [1, 2]. The results show that the nucleation can be efficiently suppressed by increasing the heating rate. A great number of nuclei form during the heating process above T_g rather than the aging process below T_g . Besides, the nuclei, which appear during heating, would be completely destroyed at a critical temperature, indicating all the influence of aging below T_g on nucleation disappears. And this critical temperature increases with the increase of aging time. It indicates that some motions in glassy iPB-1, on very small length scales, continue after the completion of enthalpy relaxation and provide a driving force for nucleation.

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Crystalline-crystalline isotactic polypropylene-based block copolymers prepared by Pyridylamidohafnium Catalyst

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A structural and morphological characterization at different length scales of crystalline-crystalline block copolymers (BCPs) formed by isotactic polypropylene (iPP) block linked to polyethylene (PE) block¹ obtained through metallorganic² catalysis is reported.

These systems allow studying of the effect of confinement on the crystallization behavior under different crystallization conditions. The final morphology of these systems is path dependent, being affected by the competition between crystallization and phase separation.

The properties of this class of materials can be tailored by combining the wide range of morphologies that develop in crystalline BCPs with the polymorphism of iPP, and choosing the proper crystallization conditions. To this aim, a detailed structural characterization has been performed for samples crystallized in the bulk, thin films and stretched fibers and stress-induced phase transformations have been also analyzed. Moreover, simultaneous time and temperature-resolved WAXS and SAXS experiments have been performed with synchrotron radiation to clarify the melting and crystallization behavior.

Finally, thin films of iPP-*block*-PE have been epitaxially crystallized onto crystals of organic substrates to achieve a control over the crystallization of both crystalline blocks. The final morphology depends on which polymer block crystallizes first, a sequence that depends on the block copolymer composition and block lengths.

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Molecular weight dependence of growth rate of spherulite of cyclic poly(ϵ -caprolactone) polymerized by ring expansion reaction

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In order to clarify the molecular weight dependence of the growth rate of spherulite G of cyclic polymers consisting of a repeating unit not including other structural units, we studied the G of cyclic poly(ϵ -caprolactone) (C-PCL) from the melt as a function of degree of crystallization temperature T_c and degree of supercooling ΔT by means of polarizing optical microscope. We prepared several C-PCLs polymerized by ring expansion reaction with different weight average molecular weights $M_w=16600, 33400, 41000, 73500$ and 84700 and linear PCLs (L-PCL) with $M_w=16000, 35000$ and 59800 . M_w was determined by GPC using linear polystyrene standards.

G of all the sample were obeyed the equation, $G=G_0\exp(-B/T_c\Delta T)$. B s of C-PCL were almost equal except for low molecular weight C-PCL. Since B is proportional to the surface free energy of the nucleus, this indicates that the regularity of folding surface of high molecular weight C-PCL is independent of M_w .

Comparing with C-PCL and L-PCL having almost the same M_w , G of L-PCL is higher than that of C-PCL at the same $T_c\Delta T$. This indicates that the entanglement of C-PCL is less than that of L-PCL. We found that the relationship of $G_0\propto M_w^{-1.4}$ holds in C-PCL and the relationship of $G_0\propto M_w^{-0.67}$ does in L-PCL. Difference in the power of M_w dependence of G_0 indicates difficulty of the sliding diffusion in the nucleus. This strongly supports that absorption behavior of C-PCL chains on secondary nucleus is significantly different with that of L-PCL.

Controlling nucleation in quasi-two-dimensional Langmuir poly(L-lactide) films through variation of the rate of compression

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Poly-L-lactide (PLLA) is considered as a “green ecofriendly material” which is widely used in diverse applications as certain properties of the material can be adjusted on demand. One of these properties is the degree of crystallinity which strongly influences the rate of biodegradation of the polymer packaging products or the controlled release of drugs from PLLA based carrier systems. In this context our work is focusing on experimental strategies to induce phase transitions in two-dimensional model systems in a well-controlled manner.

Langmuir polymer films are well suited to obtain insight into phase transitions because the density of the molecules at the surface of a Langmuir trough can be controlled precisely while other relevant parameters, e.g. the temperature and the pH value, are kept constant.

Increasing the surface density of PLLA molecules at the air-water interface induced a transition from a monolayer of widely separated molecules to a homogeneous monolayer of closely packed molecules. Upon further compression into the apparent plateau of the isotherm, the “over-compressed” quasi-two-dimensional monolayer evolves into a layer of coexisting phases *via* nucleation and growth of mesoscopic clusters, which extend into the third dimension. We found a linear correlation between the number density of these mesoscopic clusters and the rate of compression spanning a range of more than two orders in magnitude. This finding might open routes for a fine-tuning of the crystallinity in PLLA materials.

Flow induced crystallisation in polymers: from molecules to processing

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Flow profoundly influences the crystallisation kinetics and morphology of polymeric materials. By distorting the configuration of polymer chains, flow breaks down the thermodynamic and kinetic barriers to crystallisation and directs the resulting crystallisation. This flow-induced crystallisation (FIC) in polymers is a fascinating, externally driven, non-equilibrium phase transition, which is controlled by kinetics. Furthermore, the effect is of central importance to the polymer industry as crystallisation determines virtually all of the useful properties of semi-crystalline polymer products.

Simulating and modelling flow-induced crystallisation in polymers is notoriously difficult, due to the very wide spread of length and timescales. We will present results from an ongoing multi-scale modelling project. This project combines novel modelling that addresses several of the key issues affecting flow-induced crystallisation. This includes a detailed model of the non-linear flow of polydisperse linear polymers, molecular dynamics simulations of nucleation under flow from well-entangled chains and a coarse-grained model of nucleation that accounts for the wide spread of chain deformation that occurs in industrial melts under flow. We have developed these new techniques into a continuum model of polymer FIC that inherits monomer-level detail from molecular dynamics simulations but is sufficiently cheap for use in computational fluid dynamics. We will present results from this model, including a comparison with FIC data from industrial melts.

Crystallization and self-nucleation of PLA, PBS and PCL in their immiscible binary and ternary blends

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Three semicrystalline polyesters, poly(lactic acid), poly(caprolactone) and poly(butylene succinate) (PLA, PCL and PBS) were melt blended to prepare binary and ternary systems of selected compositions. Binary blends showed a sea-island morphology, while all ternary blends exhibited a “partial-wetting” morphology [1]. The crystallization and self-nucleation behaviours of the three phases have been investigated under non-isothermal conditions via differential scanning calorimetry. The self-nucleation behaviour of the polyesters in the binary and ternary blends was then compared to that of the neat polymers. It was found that the very large number of self-nuclei generated by the self-nucleation protocol (in the self-nucleation *Domain*) applied to the samples, completely overrules any effect of blend type or composition [2]. However, when melting memory is erased and sufficiently high melting temperatures are employed, the role of heterogeneous nucleation is apparent, and the crystallization of the given blend component is highly dependent on the particular morphology [2].

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The crystallization behavior of polymeric semiconducting thin film, studied by fast scanning calorimetry

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Polymeric semiconductors attract great interest for substantial applications ranging from field effect transistors to organic light emitting diode (OLED) and electronic skins.¹ These materials, commonly called conjugated polymers, have a covalently linked backbone that allows charge transport by delocalized electronic cloud and flexible alkyl side chains facilitating the solubility and stretchability. The unique molecular architecture leads to complex condense structure for bulk samples and especially for spin coated thin films, including paracrystalline fracture and multi-amorphous phases.² Till now, the structure-mechanical property relationship for semiconducting polymers is still not clear. Understanding the crystallization behavior of polymeric thin film is helpful to explain the optoelectronic and mechanical performance. Here, we used fast scanning calorimetry to study the intricate crystallization behavior of DPP-based conjugated polymer thin film. An oriented structure can still be observed after a high cooling rate of 10^5 K/s from melt, which shows a liquid crystal behavior. And, the crystallization rate and the crystallinity both decrease with the film thicknesses. Furthermore, we found that the crystallinity of as-deposited thin film is equal to that of amorphous thin film annealed at a properly temperature for several years. This indicated the importance of spin-coated process of semiconducting thin film rather than the thermal treating process.

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Isothermal Step Thickening in a Long-Chain Aliphatic Polyester

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The long-chain aliphatic polyester with 48 carbons in both the diacid and diol components (PE-48,48) exhibits two melting endotherms when it is either fast-crystallized or isothermally crystallized near and below the temperature of the first melting peak. These two endothermic peaks arise due to the presence of two populations of crystals differing in thickness, as indicated by small angle x-ray scattering. At low isothermal crystallization temperatures, PE-48,48 initially forms layered crystals containing three repeating units, corresponding to the low temperature melting peak. These thin crystals are metastable however, and with increasing crystallization time, evolve toward thicker crystals consisting of four repeating units, corresponding to the high melting peak. PE-48,48 is the first precision polyethylene known to be subject to isothermal thickening, which has been only observed previously in long-chain n-alkanes¹ and low molecular weight poly(ethylene-oxide)². The formation of two types of crystals with step difference in thickness has a profound effect on the overall crystallization rate, especially for temperatures in the transition between both forms. At high isothermal crystallization temperatures, i.e. above the temperature of the first melting peak, only crystals containing four repeating units are formed. At intermediate temperatures, there is a minimum in the heat of fusion attained for long crystallization times, indicating competition between formation of thin and thick crystals. Current work is focused on determining if the minimum in heat of fusion corresponds to a minimum in the crystal growth rate. Such a result would support a lamellar crystal growth driven by segmental deposition events, i.e. attachments and detachments of thin segments, taking place at the crystal growth front.

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Morphology and growth rate of spherulite of cyclic poly(ϵ -caprolactone) having a triazole group at closing point

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In order to clarify the effect of triazole (TR) group at closing point within the chain of cyclic polymer on the morphology and crystal growth, we studied the morphology and the growth rate of spherulite G of cyclic poly(ϵ -caprolactone) having a TR group at closing point (TR-PCL) as a function of degree of supercooling ΔT by means of polarizing optical microscope. We prepared several TR-PCLs synthesized by ring closing reaction from their linear precursors with $M_w=30000$ and 50000 , and cyclic PCL polymerized by ring expansion reaction (C-PCL) with $M_w=26000$, and linear analogue having a TR group at a chain end (TR-PCL-OH) with $M_w=26000$. M_w s of all the samples were determined by GPC using linear polystyrene standards.

We found that TR-PCL and TR-PCL-OH show banded spherulites at small ΔT and ordinary spherulites with maltase cross at large ΔT . Whereas, C-PCL only showed ordinary spherulites without banded spherulites at any ΔT . This implies that the lamella in the spherulite is twisted along the radial direction in order to relax the imbalance of stress between both end surfaces of lamella due to steric hindrance of TR group. G s of all the sample were obeyed the equation, $G=G_0\exp(-B/T_c\Delta T)$. B of C-PCL is constant irrespective of ΔT . However, B of TR-PCL and TR-PCL-OH showed two values depending on ΔT . At the region of lower B , i.e., small ΔT , the banded spherulites could be observed. The change of B corresponds to the morphological change of the spherulites. Since the lamellar thickness becomes large at small ΔT , TR groups excluded from the lamella become to assemble near the end surface of lamella. This is the reason why B becomes low at small ΔT . In TR-PCL with higher M_w and TR-PCL-OH, the decrease of B with decrease of ΔT becomes small comparing with that of TR-PCL with lower M_w due to relatively small effect of TR group.

Oriented Overgrowths of Poly (L-Lactide) on Oriented Isotactic Polypropylene: A Sequence of Soft and Hard Epitaxies

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The crystallization behavior of an amorphous poly (L-lactide) (PLLA) layer deposited on uniaxially oriented isotactic polypropylene (iPP) substrate has been studied by atomic force microscopy and electron microscopy combined with electron diffraction. A patterned PLLA structure with two fixed lamella and chain orientations was observed. Electron diffraction demonstrates that the major lamellar set is oriented with molecular chains perpendicular to the chain direction of the iPP. The minor lamellar set is inclined at ca. 64° to both the iPP chain axis direction and the lamellae of the major set as judged from both the bright field electron micrograph and the AFM image. The orientation of the main set has been explained in terms of “soft” epitaxy or graphoepitaxy, in which PLLA chains oriented parallel to the ditches of the iPP substrate caused by alternatively arranged crystalline and amorphous region. The minor set is due to a homoepitaxy of PLLA with parallelism of the helical paths. The orientation of this minor set of lamellae therefore depends on and can help determine the chirality – L or D – of the PLA investigated..

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Inhomogeneous deformation of microinjection molded PE copolymer at elevated mold temperature obtained from statistical data of tensile fracture tests

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In the present work, the fracture behavior of microinjection molded PE copolymer with weldline at different mold temperature was investigated. For each mold temperature, more than one hundred tensile tests were carried out to obtain the statistic fracture data. The results demonstrated that the probability density function (PDF) of fracture time followed Gaussian distribution at low mold temperature, which indicated the deformation was homogeneous until ultimate fracture [1]. While at mold temperature of 75 °C., the distribution deviated from Gaussian curve implying the inhomogeneous deformation. Combining with the similar results of the tensile tests for the microinjection molded sample without weld line, it was suggested that weld line or the orientation inhomogeneity as defects dominated the fracture process at low mold temperature. While defects was reinforced to a certain degree in the course of tensile stretching at elevated mold temperature, thereupon it was a comprehensive behavior between random fracture and defects dominated fracture, resulting inhomogeneous deformation till break.

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Renewable oxalamide based compounds as potential nucleating agent for biobased polymers

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Over the last decades, the fossil fuel based economy grown exponentially. However, due to the increasing demand and the depletion of fossil resources, both academia and industry focus on biobased resources as renewable feedstocks to design sustainable alternatives to petrochemical-based thermoplastics [1]. As an example, poly(ethylene-furanoate) (PEF) has proven itself as a renewable substitute to poly(ethylene terephthalate) (PET) for soft plastic bottles. Similarly, poly(lactide) (PLA), which can be synthesized from fully biobased resources, raised also interest. However, PLA has limitations like brittleness, low impact resistance and poor long-term behavior, mainly due its poor crystallinity after processing involving fast cooling rate.

To address this problem, in this work, a series of naturally occurring amino acid based bisoxalamide compounds were developed and their nucleating efficiency for both PLA and PEF was explored. In case of PLA, these additives improved the nucleation efficiency, allowing for control over both the crystallization morphology and final mechanical properties. In this work, we demonstrate that the crystallization of these oxalamide based compounds from the polymer melt imposes stresses on the surrounding polymer, thereby promoting the nucleation rate.

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Flow-Induced Crystallisation of polymers

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Flow-induced phase transitions take advantage of meta-stable states and can be of great practical and industrial value. Early work focussed on dilute polymer solutions, before extending further to encompass polymer melts. Current work on the molecular origins of flow-induced crystallisation (FIC) is providing insight into this intriguing, kinetically driven, non-equilibrium phase transition.

Previous work within this group has shown that the longest chains play a critical role in the nucleation and subsequent growth of flow-induced crystal structures. These long chains are stretched under shear flow to form 'shish', from which the bulk of the material crystallises to form lamellar 'kebabs'. A combined approach of parallel plate shear flow and small-angle X-ray scattering (SAXS) has helped to elucidate some of the key requirements for this phenomenon. A clear boundary can be observed between oriented and unoriented material which is dependent on shear rate and time. By extension, the total strain is therefore also an important factor. It has been found that the necessary conditions for obtaining oriented nuclei is proportional to the inverse Rouse time of the longest chains in the melt. Correspondingly, the mechanical work must also be greater than the critical work threshold.¹⁻² These structures are not just for academic interest. All industrial plastics processing techniques utilise flow of polymer melts to varying degrees. As such, this is a fascinating topic of interest with direct impact upon the plastics industry.

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Effect of the uncrystallizable 3-hydroxyhexanoate content on crystallization behavior of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) from the melt

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Crystallization behavior from the melt of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) has been investigated by DSC, IR spectral and X-ray scattering measurements. It was reported that PHBH formed the less ordered crystal structure before appearance of the highly ordered crystal structure. Intramolecular interaction between the C=O group and the CH₃ group of neighboring chains may be reduced along the *a* axis of orthorhombic unit cell of P3HB with temperature. In order to understand the crystallization behavior on the molecular scale, in this study, we investigated isothermal crystallization behavior from the melt of PHBHs by time-resolved wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) measurements. The effect of the 3HH content in PHBHs on their crystallization behavior was discussed in details. Samples used in this study were biobased poly(3-hydroxybutyrate) (P3HB) (Sigma-Aldrich Co., $M_w=1.20 \times 10^6$, $M_w/M_n=4.5$, and Kaneka Co.) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) (Kaneka Co.) having 3-hydroxyhexanoate (3HH) contents of 3.2, 5.8 and 10.4 mol%. The samples were isothermally crystallized at crystallization temperatures (T_c) such as 60 ± 2 and 80 ± 2 °C after rapid-cooling from the melt at 185 °C. Crystallization behavior of PHBHs was traced by time-resolved WAXD and SAXS measurements using synchrotron radiation in SPring-8 (RIKEN, Japan). The wavelength of direct beam was 0.1 nm. Diffraction patterns were detected with a Flat Panel (FP) detector for WAXD and a PILATUS 3×2M detector for SAXS. The induction time of crystallization was evaluated as the time period until Bragg diffraction appeared after the sample temperature firstly reached T_c from the melt. The magnitude of a slope in a plot of crystallinity as a function of crystallization time was evaluated as crystallization rate. It was indicated that the induction time and the crystallization rate decreased with increasing the 3HH content from 3.2 to 10.4 mol% in PHBHs. The induction time of crystallization became longer at the same degree of super cooling (ΔT) from the equilibrium melting temperature of P3HB. The details of dependence of 3 HH content and T_c on crystallization behavior and crystallization rate of PHBHs will be explained on the basis of WAXS and SAXS data.

Investigation of Structural Evolution of Polyethylene during Film Blowing

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As an important polymer film processing technology, film blowing is widely used in many fields, such as greenhouse film and mulching film in agriculture and packaging material in industry. The molecular chain structure of the raw material, the cooling and flow field during film blowing have a profound influence on the processing stability and performance of final films. However, film blowing coupled with multiple processing steps and processing parameters, which involving several non-equilibrium scientific problems, such as melt stretching nonlinear rheological, temperature-induced crystallization (TIC) and flow-induced crystallization (FIC) under the high supercooling. It is rather complicated to establish the relationship of processing-structure-properties during film blowing. In order to study the structural evolution from just exist the die to the final film, we developed a set of monolayer film blowing device combined with synchrotron radiation X-ray. The external field parameters, i.e. temperature and the movement speed of bubble, and multi-scale structural information such as crystallinity, long period and orientation can be obtained. By studying the structural evolution of two kinds of polyethylene with different topological structures under different take-up ratios, the evolution characteristics of crystal network and crystal scaffold under different external field coupling conditions are analyzed, and the interaction effects of temperature and flow field on the film blowing process are clarified. Combining with the characterization of the macroscopic properties of final films, the relationship between film processing-structure-performance in the process of film is finally constructed.

Key Words: film blowing; polyethylene; synchrotron radiation X-ray; crystallization

Confined crystallization of core-forming PEO blocks in micellar nanostructures generated during polymerization

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The nanostructuring of a block copolymer (BCP) in a polymer matrix can be produced *in situ* along polymerization, starting from a homogeneous solution of the BCP in the mixture of monomers (reactive solvent) [1]. The condition is that one of the blocks phase separates during polymerization while the other one remains miscible throughout the reaction. However, there is one aspect of this process that remains virtually unexplored, and is the fact that the demixing block can crystallize during reaction. In such a case, different nanostructures can be generated depending on the crystallization conditions [2]. In this context, a detailed understanding of the role played by the crystallization process is crucial to precisely control the morphology of the generated nanostructures.

In this work, a poly(styrene-*block*-ethylene oxide) (PS-*b*-PEO) block copolymer was dissolved in photoactivated styrene monomer, at a 10 wt% concentration. The resulting solution was irradiated for 2 h to promote the demixing of PEO blocks by reaction-induced microphase separation. Then, samples were allowed to crystallize in the dark at different temperatures (20, -5 and -15 °C). After one week of annealing, samples were fully photopolymerized at room temperature. Different crystalline-core nanostructures were generated depending on the crystallization conditions, as revealed by TEM and SAXS analysis. In view of these results, DSC scans were performed to explore the crystallization behaviour of core-forming PEO blocks within the different confined environments.

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Stretching-induced Phase Transition of the Butene-1/Ethylene Random Copolymer: Orientation and Kinetics

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The stretching-induced phase transition from tetragonal form II to hexagonal form I and the corresponding evolution of crystallite orientation were studied for the butene-1/ethylene random copolymer with 1.5 mol% ethylene by using a combination of tensile test and in situ wide angle X-ray diffraction. Three orientation pathways were distinguished for II-I phase transition, including the phase transition accomplishing within off-axis oriented crystallites (pathway 1), the phase transition with simultaneous formation of highly oriented crystallites (pathway 2), and the phase transition occurring within the highly oriented crystallites already formed (pathway 3). Except for the fact that phase transition kinetics can be significantly accelerated during stretching [1-2], we also found that the kinetics of II-I transition was correlated with the macroscopic mechanical response, which exhibits a strong dependence on orientation. In orientation pathway 1, the triggering of phase transition corresponds to the mechanical yielding in orientation pathway 1. More interestingly, the kinetics of subsequent transition exhibits the identical dependence with stress. However, in orientation pathways 2 and 3, appearance of the highly oriented crystallites substantially alters transition kinetics, which is tentatively associated to the stress bearing by the inter-stack tie chains.

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Biaxial stretch induced crystallization: An in-situ Synchrotron Radiation Wide angle X-ray Diffraction Study

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Crystallization kinetic and crystal morphologies can be greatly altered upon the exertion of flow during processing. Thus, building a quantitative model for flow induced crystallization (FIC) is essential for guiding the precise manufacturing of semicrystalline polymers. Due to the limitation of experimental conditions, the understanding of FIC is mainly based on uniaxial stretching. However, the polymer melts are subjected to multi-axial deformation during processing. With the special designed mini-biaxial stretching device, the crystallization under biaxial stretching is monitored with synchrotron radiation wide angle X-ray diffraction. The results shows that within the ratio of biaxial stretch ratio of 1.6, namely (for stretch ratio in horizontal direction, for that in vertical direction), crystallization is not observed until breakage. Comparing with the uniaxial stretching, the decrement of conformational entropy is higher for biaxial stretching, which challenges the common wisdom of the entropy reduction model proposed by Flory[1]. The contribution of chain orientation is quantified with Maier-Saupe theory, which is further incorporate with conformation entropy reduction to get the nucleation barrier under stretching. With multi-dimension linear regression, a quantitative model is established with the structural parameter from WAXD, which shows an uncertainty of 2.6%. And this model can be generalized for FIC of polymers.

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Different Nucleation Mechanism of Polyethylene under Quiescent and Flow Conditions

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The nucleation mechanism of polyethylene under quiescent and shear flow conditions are comparatively studied with all-atom molecular dynamics simulations. At both conditions, a non-classical two-step nucleation process was observed, which, however, proceed via different intermediate states. Quiescent nucleation is assisted by local ordered structures, while flow-induced nucleation is promoted by density fluctuation, which is the result of forcedly conformational and orientational transitions under an external field. At quiescent condition, the 3-dimensional random coil molecular chains transform into rigid conformational ordered segments with the help of local intra- and intermolecular interactions, which is the most peculiar and rate-limited step in polymer crystallization, while this process could be easily reached under flow. Current work suggests that acceleration of nucleation rate in orders of magnitude by flow may be attributed to the different kinetics pathway via conformational/orientational ordering – density fluctuation – nucleation.

Molecular Weight Dependency of Mesophase Formation in Isotactic Polypropylene

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Massive investigations, focusing on the crystallization temperature [1] and cooling rate [2, 3] dependency of the formation of mesophase in isotactic polypropylene (iPP), have been carried out during past decades. The influence of iPP molecular weight on the development of mesophase, however, is rarely concerned. We recently used five iPP samples with different molecular weights (M_w , from 12 Kg mol⁻¹ to 580 Kg mol⁻¹) to explore the formation of mesophase under the same quenching processes. Pure mesophase was successfully induced in iPP samples with the lowest and the highest molecular weight. The ones with moderate molecular weight were failed to form wholly mesophase. These performances were confirmed to be related to the crystallization ability of iPP samples with different molecular weights. The lowest and the highest molecular weight iPP samples always presented lower crystallization rate than the ones with moderate molecular weight, thus, it was easier for the former samples to develop mesophase. Besides, the nucleation and growth of mesophase in these iPP samples will be discussed on the basis of the flash differential scanning calorimetry results.

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Intermolecular Interaction of Substituted Poly(lactic acid) Crystals Having Isopropyl Side Chains

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Recently, increasing attention has been paid to the side-chain-substituted poly(lactic acid)s (SPLAs) to overcome the weakness of bio-based poly(L-lactic acid) (Me) such as low melting temperature. Our group has demonstrated that an SPLA having isopropyl side chains (iPr) shows higher melting temperature ($T_m^0 \approx 240$ °C [1]) compared to Me ($T_m^0 \approx 200$ °C [2]). However, the relationship between the side-chain structure and T_m^0 is yet to be clarified. In order to reveal this relationship, we investigated the intermolecular interaction in iPr crystals mainly using infrared spectroscopy (IR).

First, we assigned C–H stretching bands in IR spectra of iPr (β -form) to main and side-chain derived ones by polarized IR technique and chain conformation of iPr [3]. Time-resolved IR spectra of iPr (β -form) were measured during the heating process to investigate the intermolecular interaction. The spectra obtained showed that the C–H stretching band of side chains shifted to the lower-frequency at the elevated temperature, indicating that the C–H \cdots O=C hydrogen bonding is gradually weakened [4], and hydrogen atoms in side-chain CH groups of iPr form the C–H \cdots O=C hydrogen bonding. Since Me does not have C–H \cdots O=C hydrogen bonding [5], this hydrogen bonding in iPr should contribute to the melting temperature increase.

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Characteristic Crystallization of Cylindrically Microphase-Separated Crystalline-Crystalline Diblock Copolymers

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The crystallization behavior and resulting morphology of crystalline-crystalline diblock copolymers depend significantly on the difference in melting temperatures between constituent blocks. Sequential crystallization is observed when the melting temperatures of both blocks are sufficiently separated, whereas simultaneous crystallization may partly occur when the melting temperatures are close. In this simultaneous crystallization, characteristic behaviors such as the formation of double spherulites have been reported when the segregation force between both blocks is small [1], but there are few studies on the simultaneous crystallization when the segregation force is large, and hence details of crystallization mechanism are unknown. In this research, polyethylene-block-poly (β -propiolactone) (PE-b-PPL) was used as the crystalline-crystalline diblock copolymers, where both blocks have close melting temperatures and large segregation force. We investigated the crystallization behavior of both blocks under various conditions. Simultaneous crystallization could be achieved by confining PE blocks into a cylindrically microphase-separated structure. Furthermore, we considered the crystal structure of PPL blocks, because they take various crystal structures such as β - or δ -form with different crystallization behaviors depending on the sample preparation method [2].

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Plastic Deformation and Cavitation in the Tensile Stretching of Isothermally Crystallized Poly(ϵ -caprolactone)

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In situ small-, ultrasmall-, and wide-angle X-ray scattering measurements were performed to investigate the structural evolution of crystalline lamellae and cavities as a function of deformation ratio during tensile deformation of isothermally crystallized poly(ϵ -caprolactone). The cavities were modeled as cylinder-shaped objects which are oriented along the stretching direction and randomly distributed in the samples [1,2], and their dimensions were evaluated by direct model fitting of scattering patterns. At small deformations, the cavities occurred only in the crystalline lamellae, and the orientation of these cavities at the onset of cavity formation was related to the isothermal crystallization temperature. Upon further stretching the cavities were found to cluster in the interfibrillar regions at moderate strains where the long spacing of the newly developed lamellae along the stretching direction remained essentially constant. At large orientations the cooperative deformational behavior mediated via slippage of fibrils was evidenced, the extent of which depended on the cavity number, which could be traced back to the significantly different coupling forces imposed by chains connecting adjacent fibrils. Furthermore, wide-angle X-ray scattering results revealed that a fraction of the polymer chains with their orientation perpendicular to the stretching direction were still preserved even at large macroscopic strains.

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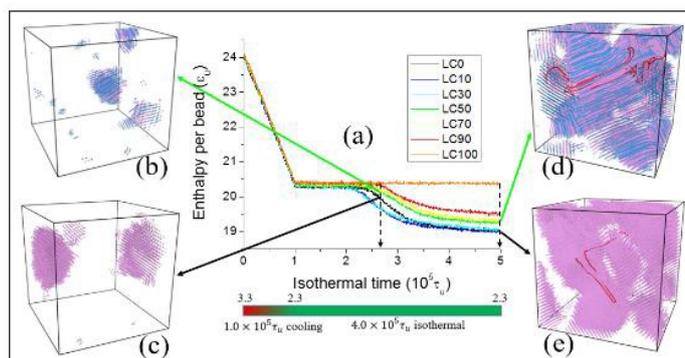
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Crystallization and molecular topology of linear semi-crystalline polymers: simulation of uni- and bimodal molecular weight distribution systems

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The crystallization behavior and the molecular topology of bimodal molecular weight distribution polymers are studied using a coarse-grained molecular dynamics model with varying weight fraction of short and long chains.



Extensive simulations have been performed to prepare polymer melts and obtain semi-crystalline polymer by homogeneous isothermal crystallization. The incubation time (the time elapsed before the establishment of steady-state nucleation) is calculated and the interfacial free energy is obtained using a mean first-passage time analysis. The incubation time first decreases with weight fraction of long chains, reaches its maximum at 30%, and then turns to increase afterwards. This results from conflicting effects of interfacial free energy and mobility of chain segments. Interfacial free energy decreases with weight fraction of long chains, which is attributed to the transition from intermolecular to intramolecular nucleation, whereas the chain mobility decreases with increasing long chain content. Nevertheless, the growth rate of crystals decrease continuously with weight fraction of long chains, mainly resulting from reduced chain sliding diffusion. We have provided insights into how bimodal molecular weight distribution polymer promotes both nucleation and processability. Moreover, a numerical algorithm has been proposed, tracing each chain going back and forth among crystallites, to access quantitative data of molecular topology (*i.e.* loop, tie and cilia segments). It turns out that the concentration of loop and tie segments increases by increasing weight fraction of long chains. This could be important to understand the mechanical properties of semi-crystalline polymer.

Self-nucleation of polyamide 11 containing nodular or spherulitically grown lamellar crystals

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The kinetics of melt-recrystallization and the stability of self-nuclei of polyamide 11 (PA 11) initially containing either nodular or lamellar crystals was investigated by fast scanning chip calorimetry. Nodular crystals formed via homogeneous nucleation during cold-crystallization while spherulitic growth of lamellar crystals was achieved by isothermal crystallization at low supercooling of the melt.

The halftime of self-seed-based melt-recrystallization of PA 11 initially containing nodular crystals was significantly shorter than the halftime of melt-crystallization at identical temperature. In contrast, melt-recrystallization of PA 11 initially containing lamellae and spherulites was not much faster than melt-crystallization, though microscopy confirmed presence of self-seed. Self-nuclei based on nodular and lamellar crystals remained in the melt up to temperatures about 12 and 7 K higher than the melting temperature, respectively.

While the higher survival-potential/stability of self-nuclei in PA 11 containing nodular crystals may be caused by their much lower melting temperature, the higher melt-recrystallization rate, compared to spherulitically crystallized PA 11, is probably related to the higher nuclei density.

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Patterning of P3HT thin films via bias-controlled scanning probe lithography and crystallization-driven phase separation

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Patterning the electronic properties of semiconducting polymers on surfaces at the nanometer scale has significant impact on their application in nanophotonics and nanoelectronics. We propose a novel concept based on bias-controlled scanning probe lithography (SPL) which permits localized oxidation of poly(3-hexylthiophene) (P3HT) crystals and enables the on-demand formation of nanoscale, nonconductive structures without visible changes in topography.^[1] The approach relies on Joule heating induced local melting and oxidation of P3HT resulting in nanoscopic nonconductive structures. Besides locally switching off electrical conductivity, this approach even allows to tune the electrical conductivity by adjusting the applied bias. Thus, we are able to generate patterns with nanometer spatial resolution and controllable conductivity within crystals of conjugated polymer through bias-controlled physical and chemical changes of the polymer. On the other hand, porous films of poly(3-hexylthiophene) (P3HT) were conveniently constructed through spin-coating of the blend solutions of P3HT and polyethylene glycol (PEG).^[2] Micron- and nano-scale pores were formed by phase separation driven simultaneously by incompatibility and crystallization, respectively. Our study offers a convenient method for the preparation of porous P3HT films with tunable large-scale pore dimensions and novel P3HT structures having pores of different diameters, which may be used for a variety of applications such as sensors and organic photovoltaics.

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The preparation of chain branching polyester by intermolecular hydrogen bonding and their crystallization behavior

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Numerous studies have shown that chain branching (CB) not only improves the melt strength of the polymer[1-2], but also improves the crystallization properties of the polymer[3]. For example, Liu et al[4] successfully prepared CB PLLA by the successive reactions of PLLA with pyromellitic dianhydride (PMDA) and triglycidyl isocyanurate (TGIC) together. However, the process took a lot of time and energy. Studies have shown that phenolic hydroxyl groups and polyester carbonyl groups could form intermolecular hydrogen bonding[5]. This provides a new idea for preparation of CB PLLA by intermolecular hydrogen bonding. Here, using 3-Pentadecylphenol (PDP) as chain branching agents of polyester by intermolecular hydrogen bonding instead of chemical method to regulate the crystallinity. The crystallization, melting behavior of CB polyester and its chain branching were studied.

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Crystallization of polylactide blended with novel functionalized oligomeric ladder –like polysilsesquioxanes

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Novel oligomeric vinylsilsesquioxanes of ladder-like double-strand backbone terminated with trimethylsilyl groups (LPSQ-Vi) [1] were functionalized by thioglycolic acid (LPSQ-COOH), methyl thioglycolate (LPSQ-COOME) and 2-mercaptoethanol (LPSQ-OH). Commercial PLA (NW4032D, NatureWorks) was blended with LPSQ-R (R=COOH, COOME, OH) in solution to obtain materials with 0.25-5 wt.% of LPSQ-R (PLA/LPSQ-R). PLA/LPSQ-R can exhibit interesting mechanical properties, with markedly increased elongation at break without a strong decrease of the yield stress [2].

The phase structure of PLA and LPSQ-R, depended on type of R and LPSQ-R content. Phase separation was observed even at low modifier content. The best dispersion was achieved for R=COOME; at 5 wt.% content small inclusions, mostly with sizes up to 100 nm, were observed. Crystallization of PLA/LPSQ-R was studied in isothermal conditions as well as during heating. In isothermal conditions the growth of spherulites was measured using PLM and overall crystallization kinetics was analyzed with DSC. A marked decrease in the cold crystallization temperature, by up to 20 °C, was observed during heating at 10°C/min. In isothermal conditions an increase of the growth rate and changes in overall crystallization kinetics were found. The effects were correlated with the composition and phase structure of the materials.

Acknowledgement: The work was supported by National Science Centre, Poland, grant No 2016/21/B/ST5/03070.

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Molecular dynamics simulations of crystal nucleation in entangled polymer melts under start-up shear conditions

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We perform molecular dynamics simulations of polymer melts consisting of sufficiently entangled linear chains (entanglements ~ 13) under shear flow. We present flow induced crystallisation of these chains under different degrees of supercooling (4%-14%) and at different values of the Rouse-Weissenberg number (20-80). Another distinct feature of this work is that we use a rheological model to contextualise our data because flow induced crystallisation and polymer rheology are strongly linked. We determine the Rouse relaxation time (τ_R) for linear polymer chains using an established rheological model at different temperatures and fit the simulation data with the Arrhenius and Williams-Landel-Ferry equations. We observe that the level of strain and stretch required to induce crystallisation increases with temperature. We find that the induction times follow a power law in shear rate and observe a more pronounced effect of flow rate for higher temperatures than at lower temperatures. Moreover, we determine that nucleation events occur relatively early in the shear transient and at a stretch value that is smaller than its steady state value. We also report the values of strain at which the occurrence of a nucleation event is most likely to happen.

2 kinds of non-spiral banded spherulites growing in amorphous films: unusual transrotational structure revealed by TEM

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Besides polymers spherulites are known for non-organic crystal growth including thin films that makes easier transmission electron microscopy (TEM). Last 30 years the growing interest for synthesis and studies of structures with unusual for condensed matter atom packing is observed (quasicrystals, fullerenes, nanotubes, etc.). This paper presents some experimental results for the formation and microstructure on the nano-, meso-, and microscale of the other less-known "**transrotational**" atom ordering discovered for diverse films of semiconductors, oxides and metals produced by different methods. We focus on the complicated crystallographic orientations for 2 types of spherulites observed. The main data are obtained by TEM, primarily bend-contour method.

It was shown earlier [1] that the growth of crystals in nanothin amorphous films (below 100 nm) is often accompanied by strong (up to 100 degrees per 1 μm) internal "crystal lattice bending" of non-dislocational nature. Up to now the phenomenon has been revealed for many substances and materials of different chemical bonding and various preparation conditions (Se-C, Se-Te, Sb, Sb_2Se_3 , Sb_2S_3 , Ge- Sb_2Se_3 , Ge-Te, Tl-Se, Cu-Te, $\alpha\text{-Fe}_2\text{O}_3$, Cr_2O_3 , Co-Pd, Re, W, amorphous metals, ferroelectrics, phase change materials and some other. For such extraordinary microcrystals the new term "**transrotational**" crystals was introduced [2] since the **translation** of the crystal unit cell is accompanied by slight permanent **rotation** (up to $\sim 0,1$ degrees per unit cell) around the axis lying in the film plane. In the rather usual case of spherulites growing in thin films the azimuthal misorientations are thus complicated by such "transrotation" and very complex textured crystalline aggregates are formed in result. We suppose that similar textures without spiral twisting can exist for polymers.

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The nature of memory effects in the crystallization of polyamides: The effects of Hydrogen Bonding

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Memory effect in polymers has attracted great attention as a unique feature, not commonly exhibited by low molar mass crystalline substances.^{1,2} The memory effect refers both to “morphological” and “kinetic” memory of a given crystalline state. After a mild melt treatment it has been shown that the re-crystallized superstructure bares a close resemblance to the one existing before melting.³ PA1012 can serve as a model for investigating the role of intermolecular interaction on self-nucleation. In this research, the melting memory effect and the microstructural factors of the polyamide were investigated from the N-H hydrogen bonding viewpoints. The three classic temperature domains were determined by self-nucleating experiments with DSC. When comparing the temperature range of the memory effect domain (Domain II) for the polyamide with different amide group density, the width of Domain II showed a linear relationship with the reciprocal of the average methylene number, which indicated dependency of memory effect on the amide group.

Keywords: memory effect, polyamide, hydrogen bonding, FT-IR

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New approach to the double melting peak of poly(l-lactic acid) observed by DSC

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Poly(l-lactic acid) (PLLA) is one of the most studied biopolymers nowadays. Due to its good performance, it constitutes an alternative to petrochemical-derived polymers. It was largely studied by differential scanning calorimetry (DSC) and temperature-modulated DSC. Nevertheless, there is an ongoing debate of what happens at the overlapping melting processes. In the present work, the experimental setups are discussed. Different modulation conditions are proposed for the study of the glass transition, cold crystallization, and the two reported melting processes. Finally, the experimental results allowed to measure the heat capacity change at the cold crystallization and a correct interpretation of what happens at the reported double melting peak of PLLA, which involves the existence of three crystalline structures.

Melting and crystallization kinetics as a tool to trace the entanglements formation in weekly entangled UHMWPE

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Since the introduction of the weekly entangled Ultra-High Molecular Weight Polyethylene (disentangled UHMWPE) [1], there was a significant effort to increase the knowledge on the characterization of the entanglements formation. So far, melt rheology was used to characterize the entangled state of the polymers produced. In this study, differential scanning calorimetry (DSC) was used to determine the melting and crystallization kinetics of disentangled UHMWPE. DSC melting and crystallization kinetics were found to be a valid tool to estimate the (dis)entangled state of the UHMWPE. It was found a good correlation between the disentangled state as depicted by rheology and the disentangled state as depicted by DSC in both melting and crystallization kinetics [2-3]. Crystallization kinetics results show that after reaching the fully entangled state, a recurrence of the original high melting peak (140 °C) was found. This result suggest a possible presence of different entanglements were formed upon equilibration for original disentangled UHMWPE. Molecular dynamic simulation also suggest the presence of different entanglements to explain the slow entanglement formation process in disentangled UHMWPE.

References

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Interfacial stereocomplexation to strengthen fused deposition modeled poly(lactide) welds

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The inter-layer stiffness of fused deposition modeled (FDM) parts is significantly impaired by the slow diffusion and re-entangling of polymer chains across filament interfacial welds in the build direction. To mechanically reinforce FDM interfaces a novel approach based on timing and spatial direction of stereocomplexation across weld interfaces is introduced via alternating deposition of enantiomerically opposite poly(lactides). Fundamental insight in the kinetics and spatial distribution of homo- and stereo-crystallization at FDM interfaces was successfully reconstructed in 2 and 3 dimensions by micrometer resolved Fourier transform infrared microscopy and synchrotron wide angle X-ray diffraction tomography. The rate of isothermal stereocomplexation and consequential interfacial stiffening increases with decreased absolute and relative molar masses. The spatial distribution of stereo-crystals is governed by the relative molar masses and the extent of inter-diffusion, not only under isothermal but also non-isothermal FDM conditions. The net local heat dosage, which depends on print speed, governs the length-scales of stereocomplexation and thus mechanical reinforcement. Interfacial stereocomplexation of poly(lactides) in FDM leads to a distinct 40% increase in stiffness and nucleation of bulk filaments, aiding in thermodynamic and geometrical stability.