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Book of Abstracts

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- P1 **Schwarzinger**: Polymer mass spectrometry ESI, MALDI and their combination with chromatography
- P2 **Hashimov**: Characterization of various multi-arm polyether polyols by Mass Spectrometry
- P3 **Kanaki**: GEPARD: An open-source solution for automated particle recognition and correlative spectroscopy for microplastics analysis
- P4 **Kehrer**: Surface Analytical Study of Polymers Functionalized with a Novel Cold Atmospheric Pressure Plasma Jet
- P5 **Kuki**: Mass spectrometric characterization of epoxidized vegetable oils for biopolymers
- P6 **Malanin**: Characterization of the metal-polymer interphase region by electron microscopy and micro- / nanoscale spectroscopy
- P7 **Malanin**: Nanochemical microscopy of polymer blends. Characterization tool comparison: AFM-IR, RAMAN, EDX
- P8 **Nagy**: Determination of polymer distribution of PTHF by HPLC-UV and kinetic study of 1,3-xylylene diisocyanate with mPEG and PTHF
- P9 **Schlattmann**: Influence of isomer structure of additives on the phase transition of thermoresponsible Poly(N-isopropylacrylamide) microgels
- P10 Santos: AFM-IR-Based Nanoscale Chemical Imaging
- P11 **Saller**: Investigation of three-component polyesters using MALDI/ToF-mass spectrometry

Internal Dynamics and Charges in Soft Materials – A Magnetic Resonance Investigation

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Relaxation NMR provides insight into the molecular dynamics over a wide range of correlation times. In particular the transverse relaxation time T_2 is sensitive to the motion of polymer chain segments. Measuring T_2 under shear in a double-cylinder Searle cell leads for entangled polymers to longer T_2 indicative of larger polymer chain segments moving freely. This must be the result of a loss of entanglements of a rearrangement resulting in longer chain segments between entanglements [1]. A recent development permits measuring under oscillatory shear varying both the shear amplitude and the frequency. Thus it could be shown that the effect of extending the relaxation time starts at a deformation of 100 for poly(dimethylsiloxane), only then the polymer entanglement starts to affected. In addition the combination of PFG NMR with NMR imaging in the same setup allows to measure flow pattern. It could be shown, that at the turning point of the oscillation for low-viscosity fluids a counterflow is observed.

The interaction of proteins and other macromolecules in aqueous solution is strongly influenced by the electrostatic interaction. For macromolecules the charge density usually is so high that a fraction is available to interact with other molecules or charged surfaces, the rest is compensated by condensed counterions. The self diffusion coefficient measured in pulsed field gradient NMR provides information of the hydrodynamic size and thus the conformation of polyelectrolytes in solution. It is on the other hand utilized to determine the hydrodynamic friction via the Einstein formula. In combination with the electrophoretic mobility determined by electrophoresis NMR the effective charge and thus the extend of counterion condensation is derived [2]. A major advantage of the NMR approach is that in any case spectroscopic information is available, so both the diffusion coefficient and the electrophoretic mobility are determined separately for each component in complex systems, permitting the study of the formation of complexes and weak binding as well [3].

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Separation of polymer mixtures and block copolymers by diffusion ordered spectroscopy

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Polymers are very complex molecules differing by topology, chain length, chemical composition as well as microstructure. In particular, the molar masses are of main interest. Size exclusion chromatography (SEC) is the most common method for the determination of molar masses. It separates the macromolecules according to the hydrodynamic radii. Therefore, this method is very powerful for analyzing single polymers. It also is able to comprehensively analyze copolymers if the complex multi detector analysis is applicable. In case of mixtures of polymers, the analysis might be limited.

The lecture will show the possibilities to analyze polymer mixtures by NMR using diffusion ordered spectroscopy (DOSY). The main focus will be the separation of the polymer mixtures as well as the determination of the molar masses. In particular, it will be demonstrated the possibility to separate polymer components of the same structure within the mixture as well as show their quantitative analysis regarding molar masses and contents. Especially, block copolymers were quantitatively analyzed by DOSY. The results were compared to SEC and online SEC-NMR. Furthermore, multidimensional experiments are demonstrated.

Xenon the explorer of free volume: applications of ¹²⁹Xe NMR in polymer science

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¹²⁹Xenon Nuclear Magnetic Resonance Spectroscopy (NMR) is an exceptional technique for studying many classes of materials. The chemical shift of xenon diffusing in zeolites, clathrates and clays can outline existing cavities and channels and provides information on their size, shape and chemical nature [1]. More recently we extended the application of ¹²⁹Xe NMR to Room Temperature Ionic liquids (RTILs), in this case the chemical shift of xenon can be correlated with the dynamic free volume and compared with data obtained with other techniques as Positron Annihilation Lifetime Spectroscopy (PALS) and Small Angle X-Ray Scattering (SAXS) [2,3].

Regarding macromolecules, ¹²⁹Xe NMR can provide different information depending upon the morphology of the polymer; for bulk polymers it is possible to determine the dimension of free volume of the amorphous phase, the glass transition temperature and eventually the diffusion coefficient [5]. In the case of porous polymers we can determine both the permanent porosity and the dynamic free volume generated by chain motion in the amorphous phase, as shown for hypercrosslinked polystyrene based nanoparticles [5].

The molecular imprinting technique is widely used for generating polymeric recognition materials with molecular recognition properties that in some cases can be compared with those of antibodies and enzymes. In these systems a hierarchical organization of pores is present. In fact the polymerization of methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) in the presence of solvent generates large cavities, once the solvent is removed. Furthermore the presence of a templating molecule (in our case bupivacaine) can decorate with molecular size pores the large cavities [6]. ¹²⁹Xe NMR spectra of molecularly imprinted polymers, synthesized varying the ratio among the different components, allow us to quantify the presence macropores, mesopores and bulk material, and to determine how each structure is connect to the others.

Finally I will show preliminary ¹²⁹Xe NMR results concerning glassy polymer membranes designed to selectively separate gas mixtures, membranes based on spherical inorganic nanoparticles isotropically grafted with long polymer chains [7].

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Automated Particle Analysis from 1 to 500 µm with a Combination of Optical and FTIR and Raman Microscopy to Determine Microplastics in Environmental Samples

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Polymers as microplastics (MP) have become an environmental threat with ubiquitous distribution. Microplastic pollutions have negative effects on the aquatic environment and probably on human health. After being released in the aquatic and terrestrial environment, polymers undergo biofouling and weathering processes, e.g. by mechanical abrasion and UV-light. That leads to smaller and smaller fragmentation into MP. Determining MP in environmental samples in the wide range from 1 μ m to 5 mm nearly quantitatively, quickly and reliably is a challenging task. We present an analytical approach with a largely automated combination of optical particle analysis, FTIR and Raman microscopy and spectral database search. This approach can determine particle sizes, particle size distributions and the type of polymer including color and shape.

The presentation describes the approach to identify and quantify MP in environmental samples in MP-free clean rooms with the use of blank samples in all steps. First procedure after purification of the sample is a three-step vacuum filtration to divide the particles in four fractions, above 500 μ m, from 500 to 50 μ m, from 50 to 10 μ m and below 10 μ m. After filtration, the particles of the different fractions are on IR transparent silicon filters [1]. For all following analyses, we use the in-house developed open-source software GEPARD [2]. GEPARD starts with an optical particle identification, which determines all particles in shape and dimension and stores their coordinates for the subsequent measurements with FTIR and/or Raman microscopy. Both methods identify the MP on the filter automatically using spectral databases. All databases include polymers, copolymers, fillers, paints and lacquers, as well as other organic and inorganic substances of both technical and natural origin. Based on the result of the spectral identification, each particle is assigned a substance.

The following example of the identification of the MP particles < 500 μ m in a water sample (117 I) from the river Warnow illustrates our approach. All particles were filtered in a 2-stage filtration process onto 4 filters, 2 with 50 μ m and with 10 μ m pore size, see Fig. 1.



Fig. 1. MP particles from a water sample (117 liters, river Warnow), distributed over 4 filters

Raman spectroscopy measured 68000 particles and fibers on all 4 filters. 407 MP particles were found, of which 305 are definitely MP from the river Warnow. 102 particles were excluded because they could have been introduced to the sample during sampling and sample preparation (the sampling device contains PTFE and silicone parts; the dyes PV23 and PB 15 are used in gloves and other disposables and the transport bottles were sealed with sealing parafilm). The distribution by polymer type and particle size is shown in Fig. 2. The most frequently found MP particles are the bulk plastics PP, PE, PET, PMMA and PS.





The presentation will show further results of the investigation of MP in different environmental compartments like water (river, sea, tap, wastewater), sediment, soil from agriculture, and beaches. For samples > 2 mm it is possible to measure MP directly on a boat or a ship on the sea with a hand-held NIR spectrometer. We will discuss the possibilities and limits of this NIR measurement by a comparison of these NIR measurements with laboratory FTIR measurements. A comparison between FTIR and Raman measurements for the identification of MP will be discussed [3]. The advantage of FTIR is a faster measurement time and often a better identification of the polymer matrix in coloured samples. The disadvantage of FTIR is the lower limit of particle size detection at 15 μ m. The advantage of Raman is the better detection of additives and dyes and the identification of particles down to 1 μ m particle size. The disadvantage of Raman is the longer measurement time and the appearance of fluorescence in case of insufficiently cleaned samples.

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Multiscale Infrared Spectroscopic Analysis of Thin Polymer Films

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Anisotropy and structural properties are essential for the physical, chemical and functional properties of materials and their surfaces and thin films. [1] Infrared (IR) polarimetry and related techniques [1-4] are the methods of choice for destruction-free multiscale structural analysis of thin films and surfaces in various environments. Of specific interest for determining spectra-structure correlations are investigations from macroscopic to nanoscopic length scales. For this purpose we use polarization dependent IR spectroscopic methods in combination with analytical and numerical calculations. In this contribution we will review recent methodic developments towards laser IR polarimetry and discuss limits of direct interpretations of measured reflection and absorption IR spectra of thin polymer and oxide films. Results from IR ellipsometric and IR microscopic polarization dependent reflectance spectra and AFM-IR nanopolarimetric absorption measurements of polyimide films (PI-2611) are compared. In detail s- and p-polarized reflectance and AFM-IR spectra are used for separation of in-plane and out-of-plane absorption components. In particular for anisotropic materials and those with strong vibrational oscillators this procedure is also helpful for identification of thin film optical effects and the determination of the material related optical properties.

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Interfacial Modification in Nanocomposites to Tailor Functionalities

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The talk will concentrate on various approaches being used to engineer materials at the nanoscale for various applications in future technologies. In particular, the case of clay, carbon nanostructures (e.g. nanotubes, graphene), metal oxides, bionanomaterials (cellulose, starch and chitin) will be used to highlight the challenges and progress. Several polymer systems will be considered such as rubbers, thermoplastics, thermoetts and their blends for the fabrication of functional polymer nanocomposites. The interfacial activity of nanomaterials in compatibilising binary polymer blends will also be discussed. Various self assembled architectures of hybrid nanostructures can be made using relatively simple processes. Some of these structures offer excellent opportunity to probe novel nanoscale behavior and can impart unusual macroscopic end properties. I will talk about various applications of these materials, taking into account their multifunctional properties. Some of the promising applications of clay, metal oxides, nano cellulose, chitin, carbon nanomaterials and their hybrids will be reviewed. Finally the effect of dewetting up on solvent rinsing on nano scale thin films will also be discussed.

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Polymer mass spectrometry at BAM with special emphasis on MALDI and ESI

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Since its introduction mass spectrometric techniques like Matrix-assisted Laser Desorption/ionization (MALDI) and Electrospray Ionization (ESI) have become indispensable for synthetic polymer analyses. Ideally, various polymer properties (monomer structure, masses, mass distribution, end groups) can be determined simultaneously. However, in real life these experiments are always affected by important structural parameters and instrumental limitations.

A short introduction focussing on latest findings with respect to ionisation principles and mechanisms will be given. Recent results from our group will be presented and efforts (e.g. by using MALDI - Imaging mass spectrometry [1]) to avoid common drawbacks of polymer mass spectrometry will be discussed. Beside molecular mass distributions, synthetic macromolecules can exhibit additional structural heterogeneities, like copolymer composition and topological alterations. In this regard, and the 2D combination of MS with different chromatographic separation techniques [2-3] were especially useful, since they reduce the complexity of polymer materials and provide additional information on otherwise inaccessible heterogeneities.



Fig. 1. MALDI-TOF mass spectrum of an EO-PO copolymer (left) and its calculated composition (right) after 2D LC-MALDI separation

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On-line benchtop correlation of molecular mass distribution and chemical composition via SEC-IR/-NMR and -QCL

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Polymers, in general, have three molecular characteristics of interest; 1) the molar mass distribution (MMD), 2) chemical composition (CC) and 3) topology e.g. branching (see Figure 1). The MMD is typically determined using size exclusion chromatography (SEC) with common SEC detectors such as the DRI detector and/or the UV detector. However, these detectors provide insufficient information on the chemistry or topology. This information is generally obtained by stand-alone methods e.g. IR and/or NMR spectroscopy.



Figure 1: Illustration of a polymer material as a cloud in the 3D space of the three molecular characteristics.

For the analysis of complex materials such as unknowns, copolymers or blends, the CC and topology are often a function of molar mass. Therefore, correlated analysis of size and chemical properties is of special interest, hence facilitating the need for on-line hyphenation, optimizing analysis of complex samples. In the on-line correlation of MMD and CC, the hyphenation of IR or NMR spectroscopy to SEC is a promising approach to obtain information. [1, 2] Hyphenating SEC to spectroscopy introduces certain intrinsic problems such as; 1) relatively low sample concentration after chromatographic separation, resulting in 2) low signal-to-noise (S/N) ratios with strong solvent signal overlapping in regions of interest for the analyte, especially with the use of non-deuterated solvents and 3) complex infrastructure for high field NMR. Therefore, the full optimization of hyphenated benchtop SEC-EC-QCL and -NMR with reference to sensitivity, selectivity and solvent signal suppression is of importance and will be presented. Previously, an on-line SEC-FTIR hyphenation using a standard FTIR spectrometer, with specially constructed flow cells and numerical solvent suppression of the solvents signals was developed. [3] To gain improved sensitivity, different infra-red light sources were explored. First results on a SEC hyphenated to a tunable external cavity quantum cascade laser (EC-QCL) in the mid IR electromagnetic wavelength range is presented, which has a factor 10⁴ higher light intensity than FTIR, but limited bandwidth. [4, 5] A benchtop 62 MHz¹H-NMR spectrometer equipped with a permanent magnet was also hyphenated to SEC, where the NMR acts as an on-line chemical sensitive detector. Typical sensitivities in the order of 100:1 for non-overloaded semi-preparative columns are obtained for PMMA and is sufficient for first applications. [6, 7]



Figure 2: (A) correlation of SEC-FTIR and SEC-EC-QCL-IR measurements of a PMMA sample. (B) Illustration of SEC-MR-NMR measurements on a PS/PMMA blend

A detailed description on the method development will be provided.

Application examples of a PS/PMMA blend and PS-b-PMMA block copolymer are given to illustrate the potential and benefits of the hyphenated techniques and the necessity for optimization.

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Column- and Channel-Based Polymer Fractionations Using Spectroscopic Methods as Information-Rich Detectors

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Information regarding molecular composition of complex polymers is important in order to fully understand materials' behaviour and properties during processing and application. The precise analysis of materials having multivariate distributions is a difficult task and a single separation/analysis method is often not able to provide comprehensive information. The present talk presents some principle ideas on the analysis of complex polymers regarding chemical composition and microstructure using advanced column- and channel-based fractionation methods [1-3].

For the characterization of the different types of molecular heterogeneity of polymers it is necessary to use a wide range of information-rich detectors in combination with advanced fractionation techniques. Preferably, these techniques are selective towards a specific type of heterogeneity.

The present talk presents some principle ideas on the analysis of complex polymers regarding chemical composition and microstructure using advanced fractionation and spectroscopic methods. The basic principles of multidimensional fractionations will be discussed and their capabilities in comprehensive molecular analysis will be highlighted. A number of applications including copolymer and microstructure analysis as well as the fractionation and analysis of polymer assemblies (micelles, vesicles) by HPLC, 2D-LC, and field-flow fractionation will be presented. The importance of advanced spectroscopic methods as online detectors will be highlighted. As one example, a quintuple detector set-up for thermal field-flow fractionation (ThFFF) will be presented, see Fig. 1 [4].



Fig. 1: Scheme of a quintuple detector ThFFF instrument [4]

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Fast (100 Hz) Reaction Monitoring of Curing Processes with Dual-Comb Spectroscopy

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Fast spectroscopic monitoring is a proven tool in R&D and production environments, where it is used to gain insight into chemical reactions. In this presentation we showcase how dual-comb spectroscopy (DCS) can be used to monitor curing reactions, where it can provide invaluable insight on the performance of coatings and adhesives.

Infrared spectroscopy is in many ways an ideal measurement technique for this application as it is capable of performing **non-invasive in-situ measurements** that provide direct information about the structure and bonding of the sample. However, many high-performance adhesives possess fast curing rates and the speed of off-the-shelf spectroscopic techniques is the limiting factor in their analysis. The spectrometer is based on quantum cascade laser (QCL) frequency comb technology, which allows for measurements on **milli to microsecond timescales** to be carried out.

The kinetic traces at two points in the spectra clearly show the time-point where the lamp was turned on. By fitting the growth and decay of these points, the **kinetic properties of the curing process can be determined**. In this case, a first-order reaction with a time-constant of 370 ms was found. The sample is a UV-triggered adhesive, which was kindly provided by DELO Industrial Adhesives (Germany). It possesses an infrared band at 1613 cm⁻¹ when uncured and a band at 1638 cm⁻¹ after curing. The maximal acquired time-resolution was 4 μ s and is used when speed is important. It results in difference spectra, where negative and positive bands indicate that a species has decreased and increased in concentration, respectively. This polymerization reaction is typically 5 seconds and 100 Hz Reaction Monitoring was possible to obtain deep insights on kinetic information.

This instrumentation based on DCS was previously validated with stepscan FTIR regarding the photocycle of bacteriorhodopsin which is a reversible process where reaction monitoring with microsecond temporal resolution is crucial [1]. Furthermore, this technique (DCS) was used for several fast combustion monitoring applications to identify gaseous specious when monitoring of high spectral and temporal resolutions are important [2].



Figure 1: Rapid (25 Hz) Reaction Monitoring with dual-comb spectroscopy on curing processes. Black before curing, red after curing



Figure 2: Trends with 100 Hz time resolution obtained from rapid reaction monitoring of curing processes.

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Application of mobile spectroscopic devices for on-site material analysis and failure detection

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With the increased development of portable and hand-held molecular spectrometers within recent years [1] new fields of applications have opened up:

- material identification of samples contained in large and non-portable components
- detection of material degradation effects and failures directly in the field

The usability and transferability of the well-established analytical characterisation techniques

- ATR-Infrared spectroscopy
- Raman spectroscopy
- NIR- spectroscopy
- UV-VIS spectroscopy

as mobile devices for in-field characterisation of multi-material composites such as e.g. Photovoltaic (PV) modules will be described and discussed.

During the lifetime of PV modules in the field (> 25years), they have to withstand environmental influences which may vary drastically depending on the surrounding climate. The weathering stability of the protective polymeric materials (backsheets and encapsulates) used in the multi-material composites is crucial for the reliability of the active PV components over the whole life cycle of a PV module.

Material identification of the polymeric compounds incorporated in the PV-modules is often an important task, especially when degradation and failures occur. While the knowledge of the bill of materials is one challenge, the detection of material degradation effects is another important issue. Both tasks can be solved by the application of molecular spectroscopic methods. Raman spectroscopy is the best suited method for the identification of the encapsulant (measurement through 3 mm glass), while NIR measurements allowed for the non-destructive determination of the composition of the multilayer backsheet. Surface degradation effects (e.g. oxidation, hydrolysis) are best detectable with FTIR-spectroscopy.



Fig. 1: mobile Raman spectroscopic system with zoom-adapter lens for larger working distances and probe head.

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The comparison of the first stages of electrochemical and chemical oxidation of aniline at different pH using vibrational spectroscopy and spectroelectrochemistry

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The intermediates of aniline polymerization, aniline oligomers, have received a lot of interest in the polyaniline (PANI) community. Electrochemical oxidation, conducted always at low pH, leads only to linear oligomers with monomer units linked in para positions linked (*p*-AO), while during chemical oxidation of aniline that is started in neutral medium, N-phenyl-phenazinium cation based oligomers (*o*-AO) are formed in addition to the linear chains (Fig. 1). It was shown, that o-AO can form also during electrochemical oxidation of aniline if conducted in neutral medium however it does not lead to PANI [1].



Fig. 1. SERS spectra of aniline oligomers formed during a chemical oxidation of aniline at pH 1 and 6.

In the presented work, we study in detail the aniline oligomers prepared under four different experimental settings: (1) Chemical oxidation with ammonium persulfate (APS) started in pH 1 (the pH changes during oxidation due to sulfuric acid being a by-product), (2) chemical oxidation with APS started at pH 6, (3) electrochemical potentiodynamic oxidation at pH 1 and (4) electrochemical potentiodynamic oxidation at pH 6. The reactions were followed in time to obtain spectroscopic kinetic data, in-situ methods including FTIR in-situ spectroscopy and Surface enhanced Raman (SERS) spectroelectrochemistry were used where applicable.

We have confirmed, that the N-phenyl-phenazinium cation is NOT the first adsorbed molecule even in the aniline oxidations in neutral medium (Fig. 1) and does not facilitate the contact between the polymer layer and the substrate.

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High resolution structural and chemical imaging of polymer materials using correlative microscopy

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Due to the variety of possible observables, the characterization of polymers greatly benefits from the combination of different analytical methods. The interconnection of data from separate methods can deliver a more comprehensive insight into the material, while having those methods available in a shared platform, accelerates the workflow significantly. In this contribution, we wish to present our multimodal microscopy solution along with a novel operating concept that seamlessly combines 3D confocal Raman imaging with other nano-analytical techniques such as SEM, profilometry, AFM or SNOM. This combination of analytical techniques allows for the characterization of phase separations in polymer blends and their wetting behavior on various substrates [1-3].

RISE microscopy, in this regard is a combination of Raman Microscopy with SEM (Scanning Electron Microscopy) imaging, a novel correlative microscopy technique which combines chemical specificity known from Raman spectroscopy with high spatial resolution scanning electron microscopy within one single integrated microscope system [4]. SEM typically is equipped with various accessories and modes of detection (SE – secondary electrons, BSE – backscattered electrons) and especially along with microanalysis tools (EDS, CL) can be a particularly powerful tool for scientific inquiry, providing information on morphology, elemental composition and crystallography. Confocal Raman imaging provides the opportunity for in depth analysis of polymorphs, soft matter and is capable of revealing detailed chemical information about composition, orientation, crystallinity, strain and anisotropies [4].

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Molecular Dynamics of Polyfarnesene as Studied by Broadband Dielectric Spectroscopy and Oscillatory Shear Rheology

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Broadband dielectric spectroscopy and oscillatory shear rheology were used to investigate the molecular weight dependence of the dynamics of bulk amorphous polyfarnesene (PF). A molecular weight dependent normal-mode relaxation process due to reorientation of the end-to-end vector, a molecular weight independent segmental-mode process caused by local chain motions and a glassy state β relaxation process associated with PF side group motions in the glassy state were observed. Extended PF chain conformations arising from tightly packed C11/C13 pendant groups reduces the probability of chain entanglements and leads to Rouse-like melt dynamics up to a critical molecular weight ~ 10⁵ g/mol. At higher molecular weights, PF behaves as an entangled polymer melt which is explicable with the reptation theory.



Fig. 1. Mean relaxation rates for the glassy state β relaxation, ω_{β} , the segmental process, ω_{α} , and the normal mode relaxation (ω_n) for PFs with different M_w vs. inverse temperature. The solid lines are fits using the VFT and Arrhenius equations. Polyfarnesene chemical structure: consisting primarily of 1,4 (cis, trans) addition products (C11 pendant groups) and ~10 mol% 3,4 addition products (C13 pendant units).

Dielectric spectroscopy measurements establish PF as a type-A polymer, whose normal mode relaxation is strongly dependent on molecular weight, providing a compliment to melt rheology for exploration of PF global chain dynamics (Fig.1). [1-3].

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Effect of biaxial stretching on the structure and dynamics of polypropylene films

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For power applications, good mechanical performance of flexible components needs to be combined with excellent dielectric properties [1]. Since production and processing is a very demanding process, tailored-made polymer design is required for matching the above requirements [2]. In this work, we discuss the thermal, structural, and dielectric properties of isotactic polypropylene films at each stage of the biaxial orientation (BOPP) process. Films from three stages of the process were investigated, namely cast, machine-direction oriented and BOPP films. Thermal properties of films and pellets were examined using differential scanning calorimetry [3]. Polarizing optical microscopy (POM) measurements were conducted to observe the crystal phase of the iPP pellets, as well as macroscopic changes in these films. The dielectric properties of the corresponding pellets and films at each stage of the BOPP procedure were examined with broadband dielectric spectroscopy (DS). Two melting peaks can be associated with two populations of crystals with different thicknesses over stretching. Dielectric permittivity of the film also deviates from the bulk value; the decrease in ε' is attributed to cavitation (i.e. the presence of air inside the films) as indicated by POM and further confirmed and analysed by small-angle X-ray scattering made in the same films. The presence of a Maxwell-Wagner process in DS was also found to correlate with the complex dynamics in the resulting film morphology. The work shows how, through polymer design, film processing and dielectric properties can be optimized.



Fig. 1. Arrhenius relaxation map combining dielectric and thermodynamic results, showing the different dynamics of iPP in the different processing steps.

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Applicability of multivariate data analysis of FTIR and IR-microscopy data of chlorine dioxide aged PE pipe materials

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Widespread application of polyolefin pipes and oxidative disinfectants in the drinking water distribution network creates the risk of premature pipe failure. Chlorine dioxide (ClO₂) are one of the most used oxidizing agent, hence its effect on the polyethylene (PE) pipe grades is a matter of interest [1]. Degradation of PE pipes in contact with ClO₂ is actively investigated with various characterization methods [2, 3], however the potential of FTIR spectroscopy is not fully exploited.

Chemometrics and multivariate data analysis [4, 5] (MVDA) of different PE grades with various aging period showed promising results to deeper understand the aging mechanism, to classify materials and to model the degradation kinetics. Distinct PE classes based on different aging behaviour have been identified with MVDA from FTIR-ATR data. Since MVDA models are highly sensitive for nonlinear kinetic changes, time of various auto-oxidative aging phases have been identified at a given aging conditions. Moreover, correlations maps between the ATR and tensile test data indicate that mechanical behaviour can be correlated to the chemical structural, at least in certain extent. In addition, an MVDA model have been developed to predict the density based on FTIR-ATR spectra of non-aged PE grades. The calculated density showed very good agreement with the measured values, including a few percent of standard deviation.

Cross-section samples of aged specimens were subjected to IR-microscopy analyses. Transmission and ATR mapping results suggest that the detected inhomogeneity and evolution of degradation products could assist well in the classification of PE materials with different disinfectant resistance. Furthermore, polymer and AO degradation product profiles have a high potential to promote the understanding of relevant aging mechanisms.

This study represents well firstly the broad applicability of chemometrics in polymer science and secondly, support the PE pipe grade characterization and development with improved performance in oxidative media.

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High-Brightness Mid-Infrared Lasers For Polymer Analysis

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Conventional optical techniques applied for polymer analysis in the fingerprint region of the mid-infrared spectral range typically rely on thermal infrared (IR) light sources. Such sources are characterized by significantly low brightness, which finds expression in poor signal-to-noise ratios (SNR), long acquisition times and insufficient spatial resolution.

By exploiting high-brightness broadband mid-infrared (MIR) laser sources, however, the limits of conventional instruments can be exceeded by orders of magnitude. The application of a spectrally tunable quantum cascade laser in a spectroscopic ellipsometry setup outperformed a state-of-the-art IR ellipsometer in terms of SNR by a factor of 290 [1]. This exceptional noise performance allowed to take high-resolution (1 cm^{-1}) broadband (900 cm⁻¹ – 1204 cm⁻¹) ellipsometry spectra in 887 ms, which in turn enabled to monitor molecular reorientation during the stretching of a 6 µm Polypropylene (PP) film at *sub-second temporal resolution* (Fig. 1.).



Fig. 1. Ellipsometry spectra of an anisotropic 6 μ m PP film recorded in a normal incidence transmission measurement. During data acquisition the film was stretched by an applied force. The predominant orientation of polymer chains in advancing levels of distortion is indicated.

Additionally, by means of a supercontinuum laser based MIR microspectroscopy setup, chemical mapping studies of a multilayer film containing PP and Ethylene vinyl alcohol (EVOH) have been achieved at *diffraction limited spatial resolution* [2]. Again the obtained results were compared to a conventional instrument – a standard FTIR microscope – which was outperformed in terms of both spatial resolution and SNR. Thus, the development of those novel techniques could open up new paths for future research in the MIR spectral range.

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nano-FTIR correlation nanoscopy of polymer materials

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Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) is a scanning probe approach to optical microscopy and spectroscopy bypassing the ubiquitous diffraction limit of light to achieve a spatial resolution below 20 nanometers. s-SNOM employs the strong confinement of light at the apex of a sharp metallic AFM tip to create a nanoscale optical hot-spot. Analyzing the scattered light from the tip enables the extraction of the optical properties (dielectric function) of the sample directly below the tip and yields nanoscale resolved images simultaneous to topography [1]. In addition, the technology has been advanced to enable Fourier-Transform Infrared Spectroscopy on the nanoscale (nano-FTIR) [2] using broadband radiation from the visible spectral range to THz frequencies.

Recently, the combined analysis of complex nanoscale material systems by correlating near-field optical data with information obtained by other SPM-based measurement methodologies has gained significant interest. For example, the material-characteristic nano-FTIR spectra of a phase-separated PS/LDPE polymer blend verifies sharp material interfaces by measuring a lineprofile across a ca. 1 μ m sized LDPE island (Fig. 1). Near-field reflection/absorption imaging at 1500cm-1 of the ca. 50nm thin film allows to selectively highlight the distribution of PS in the blend and simultaneously map the mechanical properties like adhesion of the different materials [3,4].



Fig 1. Near-field correlation nanoscopy of a thin PS/LDPE polymer film, highlighting the phase separation of the materials by nano-FTIR measurements as well as the different mechanical properties of the polymers.

Detailed analysis of measured nano-FTIR spectra even allow for obtaining statistical analysis of molecular orientation in thin films or particle density or separation in complex composite materials Thus, neaspec s-SNOM systems represent an ideal platform to characterize advanced material systems by different near-field and multi-modal AFM methods at the nanoscale.

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Characterisation of on-site aged polymers with vibrational spectroscopy in the context of heritage science.

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The stained glass windows of the gothic Naumburg Cathedral (Saxony-Anhalt, Germany) have been the object of a number of conservation campaigns throughout the 20th century. Materials applied during these campaigns, mainly synthetic coatings and glues, still remain on the monument.

Focusing on these materials, we combined laboratory analysis of 130 samples, and non-invasive spectroscopy on-site to cast light on the conservation history of the stained glass windows and to assess the suitability of different analytical methods in the context of heritage science: The uniqueness of the objects and their potentially critical condition makes handling them challenging. Therefore, non-invasive spectroscopic techniques are preferred, while sampling is limited to minimal, carefully collected quantities.

By means of FTIR and Raman microspectroscopy, we were able – without prior preparation – to obtain information from small samples, often containing mixtures of polymers and other organic and inorganic components. Additional insight in the composition and properties of the polymers was gained by Py-GC-MS and DSC on selected samples.

Non-invasive identification of these materials on-site was successful with use of the mobile FTIR spectrometer Alpha and the handheld Raman spectrometer Bravo, both by Bruker. The two methods complement each other and proved particularly useful in the investigation of the stained glass windows when combined.

The identified synthetic polymers, poly(meth)acrylate-based materials and epoxy resins, reflect the advances in conservation science throughout the 20th century. Having remained for several decades on site, they moreover offer an opportunity to evaluate the effects of natural, long-term weathering on synthetic polymers.

Quantum Cascade Laser (QCL) based IR Imaging and handheld mobile Spectroscopy

The new Generation of spatially resolved IR Spectroscopy and Microscopy for the Analysis of Microplastics

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Debris in the marine environment can be either natural, such as floating vegetation or volcanic ash deposits, or man-made. The man-made human sources cover the whole gamut of material types, from sewage, glass, mineral, fabric and, of increasing concern, plastic or polymeric. Virtually all plastics absorb infrared (IR) in a highly selective manner, making their infrared spectra a useful qualitative diagnostic. The triage of the visible micro (~1 mm to 5 mm), meso, macro or mega particles with portable and handheld FT-IR enables rapid determination of the material on-site, and reduces time wasted on non-polymers on-site or at site.

The brand-new QCL IR imaging technology represented by our LDIR 8700 IR system is a fast, intuitive and accurate tool for the automated analysis of microplastics. Obtaining information about ID, particle amount and size you get a complete set of information about your microplastic sample





Failure analysis of polymeric composites by FTIR-ATR-Imaging

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Attenuated total reflection (ATR) Fourier transformed infrared (FTIR) imaging was found to be a suitable analytical tool to (i) determine the chemical composition of surfaces (including potential impurities or foreign substances), (ii) detect ageing induced chemical changes on surfaces upon stress impact [1] and (iii) identify the bill of materials and chemical composition of individual layers in multi-material composites [2] (including the detection of material inhomogeneities). For the measurements, close direct contact of the ATR-crystal with the sample is mandatory (flat, plane-parallel surfaces are required). As the penetration of depth of the IR-beam into the sample is only 1-2 μ m in the MIR region, the resulting reflection spectra contain only information of the outermost surface layer. The analysis can be performed directly on a surface or a cross-section of the sample (e.g. multilayer coating or foil, multi-material composite or construction part).

Several examples of complex analytical problems - in specific in respect to failure analysis, degradation behaviour or material identification of small particles or thin layers (micron-range) – and their spectroscopic solution will be presented.

As a specific example, ATR-images taken in the course of a failure analysis of a multi-layer composite showing weathering induced cracking are shown. After identifying the area of interest (crack region) by light microscopy, ATR-images (300µm x 300µm) consisting 36864 individual spectra were taken from the selected sample region. Averaged spectra of the different layers of the cross-section were extracted from the images. For the evaluation, the ATR-FTIR images were on the one hand treated with principle component analyses (PCA) resulting in a false colour representation, where each spectroscopic distinguishable component (e.g. EVA, PA, PA-PP, glass fibre fillers, embedding resin; middle row) is displayed in a different colour. On the other hand, the images were analysed by using an intensity distribution image of the carbonyl band at 1710cm⁻¹ (degradation indicator).

The ATR-FTIR images were recorded on a Perkin Elmer Spotlight 400 equipped with a liquid nitrogen cooled MCT - linear array detector). The ATR-FTIR imaging system used comprises of a germanium (Ge) crystal with a flattened tip (d ~600 μ m).



Figure 1: Light microscopic image (top), ATR-image after PCA (middle) and intensity distribution image of the carbonyl band at 1710cm⁻¹ (bottom) of a cracked polymer composite

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Hyperspectral Infrared Laser Ellipsometry For Polymer Film Analysis

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We present a novel infrared (IR) ellipsometer for fast, highly spectrally and laterally resolved thin film analysis [1, 2]. The ellipsometer uses a single-shot design with four parallel, synchronized polarization-state detection channels, and a quantum cascade laser that is broadly tunable between 1318–1765 cm⁻¹ at speeds of up to 1500 cm⁻¹/s. The device enables phase and amplitude measurements with unparalleled time resolutions of ≤ 100 ms in spectral and $\leq 200 \ \mu s$ in single-wavelength mode. Fast hyperspectral mapping of large sample areas (50 × 50 mm²) is possible within several tens of minutes, achieving 120 μm spatial and $< 0.5 \ cm^{-1}$ spectral resolution.

IR phase and amplitude data of organic and biorelated thin films can be correlated with numerous sample properties, such as thickness, molecular structure and interactions. Analyzing the IR vibrational fingerprint, we apply the ellipsometer for time-resolved and hyperspectral studies of the chemical and structural properties of various thin films, such as thermoresponsive polymer(*N*-isopropylacrylamide) [PNIPAAm] layers (see Fig. 1).





Future applications of the ellipsometer are comprehensive process and quality control, rheology and relaxation studies, analysis of structured, anisotropic films and biological surfaces, as well as microfluidic studies of functional, sensor and biocompatible surfaces, for example, reaction and adsorption kinetics at solid–liquid interfaces.

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Monitoring the Thickness Distribution of Ultrathin Printed PEDOT:PSS Layers by NIR Hyperspectral Imaging

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Poly(3,4-ethylenedioxythiophene) (PEDOT) is a well-known conductive polymer with excellent transparency, high conductivity and high chemical stability. Due to its very poor solubility, processing of this polymer is extremely difficult. This can be at least partly overcome by synthesis of a polyelectrolyte complex with another ionomer such as polystyrene sulfonate (PSS). The resulting macromolecular salt known as PEDOT:PSS forms stable aqueous suspensions, which can be applied by a wide range of processing methods such as spin coating, gravure printing, ink jetting, slot-die coating or with a doctor blade. Similar to pure PEDOT, the layers of PEDOT:PSS show extraordinary conductivity and transparency.

For an effective control of such coating and printing processes, particularly for control of the applied thickness, continuous monitoring of the properties of the deposited layers is inevitable. White-light interferometry allows measurements with very high precision but is of limited suitability for space-resolved investigations, especially if large areas have to be scanned. In this contribution, it will be shown that NIR hyperspectral imaging is a powerful method for such investigations in spite of the very low thickness of conductive polymer layers. In particular, the thickness of thin layers of PEDOT:PSS in the range between about 60 and 330 nm was predicted from spectral data.

The reflection spectrum of PEDOT:PSS layers does not contain bands, but consists of a moderate slope of the overall reflectance in the range between 1320 and 1850 nm. Despite the low thickness, the spectra show an extremely strong dependence on the thickness of the layers, which allows their use for quantitative measurements. The prediction of quantitative thickness data from the reflection spectra was based on chemometric models using the partial least squares (PLS) algorithm. Calibration was carried out by means of spin-coated layers of PEDOT:PSS, whose thickness was determined by white-light interferometry, ellipsometry and stylus profilometry. Finally, this resulted in calibration models with root mean square errors of prediction (RMSEP) of less than 10 nm. After external validation, these models were used for quantitative imaging of the thickness distribution in PEDOT:PSS layers (see figure). The precision of the predicted values was confirmed by

from the reference



comparison with data methods.

Finally, it was shown that this approach can be also used for hyperspectral imaging of the thickness of thin gravure printed layers and structures of PEDOT:PSS applied to polymer films or paper with excellent thickness resolution. This analytical approach opens new possibilities for in-line process control by large-scale monitoring of thickness and homogeneity of ultrathin layers of conductive polymers.

Mass-remainder Analysis (MARA): a multifunctional tool for characterization of copolymers and copolymer blends

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Mass spectrometry has become an important tool for copolymer analysis, however most of the resulted spectra are extremely complex [1]. Therefore, manual assignation of all the peaks is not feasible. Suitable data handling procedure is required to handle such a data set. However, the resolution and mass accuracy may be limited by the instruments in the desired molecular weight range, demand a robust method. Mass-remainder Analysis [2, 3] (MARA) our recently developed data mining procedure was successfully applied to identify copolymer composition by medium resolution mass spectrometer. The mass remainders are simply calculated by the division of measured m/z by one of the exact mass of one repeating unit, hide the difference among molecules varying only in the selected base unit. That type of mass filtering can be improved by multiple steps. The sequential calculation of remainders makes available the further simplification of mass remainder plots of copolymer-copolymer blends.



Fig 1. Mass remainder (MR) VS *m/z* plot of PO/EO/PO triblock copolymer. The size and the colour of the bubbles are indicating the intensity and EO content, respectively.

Herein, we demonstrate the capability of Mass-remainder analysis for mapping of spectra of copolymers and copolymer blends. The visualization and identification of copolymer blends has been achieved for PE/RPE type poloxamer system and ethylene-oxide/propylene-oxide lactic acid/caprolacton copolymer blend.

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in-situ-ATR-FTIR Spectroscopy at Polyelectrolyte Based Coatings

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in-situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is a powerful tool to characterize polymer coatings at inorganic model substrates [1]. In this contribution we summarize various analytical options and examples of *in-situ*-ATR-FTIR spectroscopy at polyelectrolyte based coatings in the life science application field.

At first the ATR-FTIR detection concept based on trapezoidal internal reflection elements (IRE) housed by thermostatable in-situ (flow) cells, which are located in a multi-mirror attachment, is given. ATR-FTIR measurements are performed by the single-beam-sample-reference (SBSR) concept [2], according to which the IRE is devided into separate sample (S) and reference half (R) allowing appropriate spectral background compensation and signal to noise ratio. Experimental options are given including:

-Coated S and uncoated R both in contact to solvent or air resulting in spectra on dry or wet PEL coatings with constant or decreasing wet-adhesiveness (kinetics) under spectral compensation of IRE material.

-Coated or uncoated S in contact to PEL solution and coated or uncoated R in contact to solvent resulting in (kinetic) spectra on increasing adsorbed PEL amount under spectral compensation of IRE or coating material.

-Coated S loaded by further compounds (drugs, proteins etc) and coated or uncoated R both in contact to solvent (release medium) resulting in (kinetic) spectra on decreasing compound amount under spectral compensation of IRE or coating material.

Furthermore, temperature dependent measurements on thermoresponsive PEL coatings and dichroic measurements using IR light with P- and S-polarisation (automatic polarizer) on oriented PEL coatings can be performed.

Secondly, exemplary results on single and mixed polyelectrolyte (i.e. polycation/polyanion) based coatings with respect to deposition, composition, wet-adhesiveness [3-5], conformation and orientation [6-9] are given. Thirdly, selected results of life science application studies on the interaction of polyelectrolyte coatings to proteins [10-16] and drugs [17-20] are shown.

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Polymer mass spectrometry - ESI, MALDI and their combination with chromatography

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Polymer mass spectrometry has gained much interest in the last couple of years as it is a technique that can give a valuable insight into the chemical structure of polymers. However, the interpretation of the data is usually very complex and time consuming, especially if polymers are made up from more than one monomer and their molar mass distribution is broad.

In order to minimize the overlap of data it is beneficial to separate the polymer (mixtures) by a different separation mechanism before subjecting to MS analysis. Liquid chromatography techniques have proven to be valuable and depending on the separation column the polymers can be separated either by size or chemical composition. Unfortunately, not all chromatography setups can be combined with all MS ionization techniques and it will be the focus of this talk to point out different combinations that can be used for e.g. styrene copolymers or modified polyglycols.



Fig. 1. HPLC chromatogram of a polyethylene glycol and high resolution Orbitrap mass spectrum of singly and doubly charged oligomer eluting at 6.64 min.

Characterization of various multi-arm polyether polyols by Mass Spectrometry

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Mass-Remainder Analysis (MARA) [1], a data mining procedure, allows to handle different fragment series of complex tandem mass spectra. We will demonstrate the application of Mass-Remainder Analysis to differentiate and identify fragment series obtained from polypropylene-oxide (PPO) initiated by sorbitol. More than 20 types of fragment ions were identified. The Mass Remainder (MR) vs m/z plot is sown in **Figure 1**. The fragment series differ only in the number of monomer units have identical MR values, classifying the product ions and making the determination of the elemental composition simpler. Product ions originate from the fragmentation of linear PPO arms give only a small portion of fragment series, most of them are produced by the fragmentation of the initiator moiety [2].



Fig. 1. MARA of the filtered mass spectra of sorbitol-initiated PPO

Beside the investigation of homopolymers, ethylene-oxide/polypropylene-oxide copolymer was also studied. The presence of ethylene-oxide monomer units increased the number of fragment ions, resulting more complex spectra and multiple overlapping series.

Furthermore, we investigated the energy dependent fragmentation of linear, glycerol and sorbitol initiated polypropylene-oxides. The survival yield method was used to determine the characteristic collision energy (CE_{50}) values of these polymers.

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GEPARD: An open-source solution for automated particle recognition and correlative spectroscopy for microplastics analysis

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Microplastics, synthetic polymer particles of size between 1µm and 5mm, have proven to be an omnipresent type of environmental pollution. This finding gives rise to questions concerning their origin, distribution and fate, but also potential health risks stemming from their presence. Addressing these questions requires high-throughput analysis of environmental samples to acquire information about composition, size and abundance of microplastics.

Our in-house developed software GEPARD¹ (Gepard-Enabled PARticle Detection) offers a set of tools that largely automates the various steps involved in the identification and quantification of microplastics by Raman and FTIR microspectroscopy, hence speeding up the process.

In the example of a soil sample from the test field "Rinkenbergerhof" at the Agricultural Investigation and Research Institute (LUFA Speyer, Germany), we illustrate the GEPARD workflow, including particle recognition on the optical image of the processed sample, FTIR or Raman measurement of the particles, analysis of the spectroscopic data, and particle statistics to identify and quantify microplastics on the sample.

GEPARD is an open-source project under GNU General Public License, that can be downloaded and modified freely.

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Surface Analytical Study of Polymers Functionalized with a Novel Cold Atmospheric Pressure Plasma Jet

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In the last decades atmospheric pressure technologies have been developed as one of the most important methods for activation and functionalization, and therefore improving the wettability and adhesion properties of almost any material surface. This is especially interesting for polymers (e.g. polyolefins), featuring low surface energy and bad adhesion properties after the manufacturing [1,2]. The major advantage of atmospheric among low pressure plasma systems is that no expensive and time consuming vacuum equipment is needed. Next to corona and dielectric barrier discharges, atmospheric pressure plasma jets (APPJ) gain more and more importance. The ability to treat complex shapes, the possibility to treat specific parts selectively and a simple installation into existing production lines are compelling reasons for using APPJ systems. Reactive oxygen and nitrogen species (RONS) (e.g. atomic oxygen, OH, O3, etc.) created in the plasma effluent (see also fig. 1) are considered as most important for subsequent surface reactions, whereby the concentration and composition of this "RONS-cocktail" depend on many parameters, like working distance, gas composition, energy input or temperature.



Abbildung 1: Prinzip der Plasmaerzeugung im CAPPJ System aus Gasen und Flüssigkeits-Gas-Gemischen.

Furthermore, polymer plasma functionalization depends on the "RONS-cocktail" and the surface chemistry. The APPJ system used in this work features a novel and unique setup to moisten the process gas, enabling high concentrations of admixed water into from 0 to 100%. process gas In order to study the the complex plasma-polymer-surface-interactions for this new APPJ system, various highly surface sensitive analytical techniques like X-ray photoelectron spectroscopy (XPS), also in combination with chemical derivatization methods, atomic force microscopy (AFM), surface free energy measuremetns (SFE) were applied on several treated polymers. One of the results of our work is that a very high SFE on APPJ treated polymers always implies the formation of a layer of water soluble low molecular weight oxidized material (LMWOM) on the surface. Water admixtures significantly change the "RONS-cocktail" of the APPJ effluent, which lead, depending the process gas and on the polymer type, to different surface functionalization. E.g. air-water-mix plasma treatment on polypropylene creates rough surfaces with water resistant oxidation products, while by sole air, N2 or N2-water-mix plasma treatment most the incorporated oxygen exists as water soluble LMWOMs on the surface (see also fig. 2.) [3].



Abbildung 2: Der Einfluss von Wasser Beimischungen zum Prozessgas auf die Oberflächenchemie und Topographie von plasmabehandeltem Polypropylen [5].

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Mass spectrometric characterization of epoxidized vegetable oils for biopolymers

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Vegetable oils, such as soybean, sunflower and linseed oils, are one of the most important sources for biopolymers. Double bonds in the unsaturated fatty acids of the triglycerides can be converted to the more reactive epoxide functional groups to facilitate the polymerization process. The characterization of the triglyceride oils is essential for the design of new materials and for the quality control in the biopolymer production. The main aim of our work was the chemical structure evaluation of the epoxidized soybean and linseed oils using soft ionization tandem mass spectrometry (MS/MS).

MALDI-MS and ESI-MS were used for the characterization of epoxidized soybean and linseed oils [1]. The recently invented data mining approach, the *Mass-remainder* analysis (MARA) was implemented to the analysis of these types of complex natural systems [2]. The number of carbon atoms and epoxide groups in the epoxidized triglycerides was determined. The epoxidized fatty acid compositions of these types of oils was estimated by means of MS/MS without any complicated and time-consuming sample preparation, derivatization, or separation. It can be particularly useful in the characterization of the fatty acids variety of complex vegetable oil mixtures.

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Characterization of the metal-polymer interphase region by electron microscopy and micro- / nanoscale spectroscopy

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Epoxy resins are widely used industrial materials, with a broad scope of applications including the matrix component of corrosion-protection paints. The long-term performance (e.g. the adhesion and delamination of coatings) is assumed to depend on the existence and properties of the interphase - chemically and physically distinct polymeric region adjacent to interface with inorganic (e.g. metallic) substrates. However, the mere existence of such interphase region is frequently disputed. Little is known about the formation mechanism and extent of such boundary regions.

Our goal was to prove or disprove the existence of interphase in diglycidyl ether of bisphenol-A (DGEBA) cross-linked with triethylenetetraamine (TETA) on gold or iron substrates.

We studied thin films on the metals by ATR-FTIR and cross-sections of cellulose acetate/40 nm Fe/epoxy sandwiches by EFTEM, EELS, STEM-EELS and STEM-EDX. Possible chemical gradients and changes of local thermal properties in the sandwiches were examined by both AFM-IR and nanothermal analysis as well.

The combination of EDX, EFTEM, EELS and AFM-IR demonstrates the non-existence of micron scale interphase in TETA-crosslinked DGEBA coatings on iron. No evidence was found for extensive organometallic formation by amine complexation, see also [1]. Epoxy-group excess in thin films develops as a result of amine consumption at the air-polymer interface. The residual epoxy quantity / content measured in thin films does not correspond to a chemical gradient associated with an interphase structure. AFM-IR analysis was, for the first time, applied to acquire extremely high lateral resolution infrared spectra and maps of polymer/metal interphase regions [2].

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Nanochemical microscopy of polymer blends. Characterization tool comparison: AFM-IR, RAMAN, EDX

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Nowadays, polymer science uses a variety of spectroscopic methods to characterize physico-chemical properties in order to investigate the chemical structure of a material in the micro- and nanometer range. Sometimes it is rather difficult to evaluate the most informative and at the same time the fastest and efficient tool, because sample preparation requirements of a particular one can play an important and crucial role to obtain a suitable result.

In this study the main focus is the comparison of characterization methods such as AFM-IR [1], Raman microscopy, and EDX, as the main and the most informative tools to obtain extensive and comprehensive chemical information about a polymer blend system at the nano scale.

Polymer blends based on thermoplastic polyurethane and polyethylene as well as based on polycarbonate and poly(stryrene-acrylonitrile) were used for this study. The materials have been microtomed to obtain the thin slices (ca. 300 nm thickness for AFM-IR, 10 μ m and 20 μ m for Raman) and afterwards were deposited onto a flat solid substrate (ZnS for AFM-IR, glass for Raman) prior to be measured. The contact mode AFM-IR system Nano IR 2 (Anasys Instruments / Bruker Nano Surfaces) and the Raman Imaging system alpha 300R (WITEC) were applied. For SEM-EDX, the flat surface on the bulk piece after cutting was used – the so called blockface. The blockface was glued on a SEM holder and coated with ca. 20 nm carbon to prevent charging in the electron beam and measured using the Zeiss Ultra SEM combined with the Bruker 5060F EDX.

Parameters of the above characterization methods such as lateral resolution, component visibility and phase morphology of polymer blends as well as analysis of time consumption, measurability and influence of specific artefacts in data acquisition were compared and discussed.

For the investigated blend systems, Raman microscopy is found to be the most efficient tool to characterize the blends at the nanoscale, providing a good balance and compromise between time consumption for sample preparation and analysis results. Contact mode AFM-IR and EDX provide beneficial spatial resolution (ca. 50 / 10 nm of AFM-IR / EDX vs. 300 nm of Raman). However, sample preparation for contact mode AFM-IR is too laborious and time consuming and EDX measures only the presence and quantity of elements, but cannot provide any information about bonding of the elements. To compete with Raman microscopy, using the tapping mode AFM-IR system can be perspective and recommended.

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Determination of polymer distribution of PTHF by HPLC-UV and kinetic study of 1,3-xylylene diisocyanate with mPEG and PTHF

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We focused our attention on the reaction of 1,3-XDI with industrially important polyols such as polyethylene glycol (for the reactions the monomethoxy derivative was used, mPEG) and polytetrahydrofurane (PTHF). The reaction of 1,3-XDI with the PTHF yielded products that were each separated by HPLC according to their total number of repeat units of PTHF. First, for the sake of simplicity, these individual, separated peaks were correspondingly summed to get molar fractions of XDI 1,3, XDI 1,3PTHF and XDI 1PTHF, 3PTHF. The distribution of the oligomers as a function of the number of repeat units was required for the determination of the reactivity of the individual chains. The electrospray ionization (ESI) may give some information about it but it is feared, that the distribution may suffer from non-equal ionization efficiency for all oligomers present in the sample and/or mass discrimination effect caused by the MS detection system. So another appropriate method was applied to determine this data. In this way, all PTHF chains were reacted to form urethane (using phenyl isocyanate), which were then separated by HPLC and the individual oligomer chains with urethane end-groups were detected by UV. In the UV spectrum the oligomers with number of repeat units n = 2, 3, 4and 5 were separated and using the UV areas the molar fractions of these oligomers were found to be 0.33, 0.39, 0.21 and 0.07, respectively.

Then the reaction rate constants of the reaction of 1,3-xylylene diisocyanate (XDI) with mPEG and PTHF were determined. The polymer was employed in high molar excess to 1,3-XDI in order to obtain pseudo first-order kinetics. The values of k_1 and k_2 were found $(2.64\pm0.03)\times10^{-3}$ min⁻¹, $(2.45\pm0.03)\times10^{-3}$ min⁻¹ for mPEG and $(1.13\pm0.01)\times10^{-2}$ min⁻¹, $(1.28\pm0.01)\times10^{-2}$ for PTHF, respectively.

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Influence of isomer structure of additives on the phase transition of thermoresponsible Poly(N-isopropylacrylamide) microgels

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Thermoresponsive polymers bear a large potential for drug delivery applications, however, the influence of small molecules on the phase transition is a critical issue. Our work investigates the effects of different additives such as structural isomers of hydroxybenzaldehyde (HBA) on the phase transition behaviour of а poly(N-isopropylacrylamide)/N,N'-methylenebisacrylamidemicrogel. (PNiPAM/BIS) Different methods such as NMR Spectroscopy, Differential Scanning Calorimetry (DSC), Turbidimetry, Isothermal Titration Calorimetry (ITC) and Dynamic Light Scattering (DLS) are used to determine the characteristic Volume Phase Transition Temperature (VPTT), transition widths and critical concentrations of cosolutes.

The homopolymer of PNiPAM has already been studied earlier in the presence of various aromatic additives.^[1] In the present work, the influence of *ortho-*, *meta-* and *para-*HBA on the VPTT on a PNiPAM microgel is determined systematically and compared to a homopolymer. Those model drug substances cause a shift of the VPTT to lower temperatures, which is observed by all utilized techniques. Furthermore, as a result from temperature dependent ¹H-NMR spectra, this work proofs the existence of an incorporated species of the additives at T > VPTT. A quantification of the incorporated additive fraction is achieved. By investigation of the transverse spin relaxation times T_2 of the aldehyde protons, additive molecular dynamics below and above the collapse temperature of the microgel (Fig. 1) are clarified:



Figure 1. Illustration of local additive dynamics (sites) inside and outside a PNiPAM microgel particle at different temperatures, resulting from temperature-dependent spin relaxation times T_2 .

Three sites are identified in the microgel dispersion: a freely moving, a motionally hindered and a completely incorporated species are coexisting.

In addition, the influence of the substitution pattern of HBA and Dihydroxybenzene (DHB) on the VPTT of further acrylamide polymers is studied.

Currently, ongoing studies investigate the influence of further additives by varying the size of the aromatic π -system and by the use of additives exhibiting hydrogen-bridge acceptor/donor properties.

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AFM-IR-Based Nanoscale Chemical Imaging

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Mid-infrared (IR) spectroscopy is a well established method for analysis of polymers due to its ability to provide molecular specific IR information non-destructive, quickly and with little sample preparation. However, conventional IR spectroscopy is limited to spatial resolutions of several microns, thus preventing its meaningful application to samples with nanoscale components. This is where atomic force microscopy-infrared spectroscopy (AFM-IR) comes in. In AFM-IR a pulsed IR laser is aimed at the sample area under the AFM tip. The thermal expansion is detected by the AFM cantilever in the near-field region allowing spatial resolutions below the diffraction limit and down to 20 nm.

Tuning the laser wavelength while keeping the AFM tip in one location provides local infrared spectra. Scanning the AFM tip while keeping the laser wavelength constant provides infrared absorption images and AFM topography images, concurrently. Infrared bands can be assigned to vibrations of functional groups using well established spectra-structure correlations, taking advantage of the direct comparability between the AFM-IR obtained photothermal induced resonance (PTIR) spectra and their far-field FTIR counterparts. AFM-IR has successfully been applied to biological, inorganic and organic samples such as polymer films and fibres.

In this work, we demonstrate the application of AFM-IR to a polymer sample a sample consisting of a mixture of three different polymers was analysed, the three chemically different domains. The three different polymers were identified through their AFM-IR spectra and their spatial distribution was determined at nanoscale resolution.



Fig. 1. Schematic representation of an AFM-IR set-up using top ilumination

Investigation of three-component polyesters using MALDI/ToF-mass spectrometry

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The polymer class of polyesters (PES) offers great versatility due to variations of numerous suitable monomers, differences in the incorporation within the polymer chain and molecular mass distribution. Polyesters are well known for products like bottles and fibres (e.g. polyethylene terephthalate, PET), but are also widely used as binders for coatings or inks. Such binders are usually optimized for different substrates or application techniques and, thus, previously mentioned variations and their investigation on material properties are crucial [1].

A powerful technique for structural investigation of such polyesters is MALDI/ToF-mass spectrometry (MS). While terminating groups are usually quantified by titration and molar mass distributions observed by gel permeation chromatography (GPC), MALDI/ToF-MS combines this information and provides additional structure elucidation. As shown in Figure 1a for a two-component polyester, not only terminating groups were obtained in MALDI/ToF-MS spectra, but also cyclization of polyesters occurred.



Fig. 1. Detail of MALDI/ToF-mass spectra of a 2-component (a) and a 3-component polyester (b). Terminating groups could be identified and assigned and comonomer incorporation was verified.

For polyesters with three or more components (Figure 1b), different main series could be observed which verify incorporation of all monomers into the polymer chain. MALDI/ToF-MS not only allowed detection of terminating groups and monomer incorporation qualitatively, but quantification was tested by integrating resulting m/z signals. Here, two different modes of Time-of-Flight (ToF) detection could be used. A linear detector enhanced consistent peak integration for quantification while the use of a reflectron yielded higher resolution and mass accuracy.

1. U. Poth, Polyester und Alkydharze, 1st ed.; Vincentz Network: Hannover, Germany, 2005.