CPP 13 POSTER New Experimental Techniques

Time: Tuesday 17:00–19:00 Room: P3

CPP 13.1 Tue 17:00 P3

Measurements of interfacial viscoelasticity with the quartz crystal microbalance: influence of acoustic scattering from a small crystal-sample contact — •Alexander Martin König, Mathis Düwel, Binyang Du, Miriam Kunze, and Diethelm Johannsmann — Institute of Physical Chemistry, Clausthal University of Technology,Arnold-Sommerfeld-Str. 4, D-38678 Clausthal-Zellerfeld

We discuss the influence of the limited contact size on measurements of high-frequency interfacial viscoelasticity performed with a combination of the quartz crystal microbalance (QCM) and the Johnson-Kendall-Roberts (JKR) apparatus. In this instrument, a sphere-plate contact is established between an elastomeric lens and a quartz resonator. The analysis is carried out in the frame of the sheet-contact model, which states that the shift of resonance frequency and bandwidth both are proportional to the contact area as long as the contact area is much smaller than the crystal itself. In particular, the ratio of the shift in bandwidth and the shift in frequency (termed D-f ratio) is predicted to be constant and independent of geometry. However, the experiment does show a slight increase of the D-f ratio with contact radius when the contact radius is comparable to the wavelength of sound inside the crystal. This effect can be explained by acoustic scattering.

CPP 13.2 Tue 17:00 P3

High sensitiv AC chip calorimetry for nanogram samples — •H. Huth, A. Minakov, and C. Schick — University of Rostock, Institute of Physics, Universitätsplatz 3, 18051 Rostock, Germany

The combination of silicon technology and calorimetry opens up new possibilities. Thin film calorimeter allow heating and cooling at rates up to 10.000 K/s. For several fast crystallizing polymers it is possible to prevent crystallization on cooling totally and to reach the amorphous glassy state. But often one would prefer to measure thermal properties of small samples at or at least close to thermodynamic equilibrium. This can be achieved by a combination of chip calorimetry and AC calorimetry at slow scanning or at constant bath temperature. The frequency chosen provides a well defined time scale of the experiment. A direct comparison with results from other dynamic methods like dielectric spectroscopy is possible. Based on a differential AC-calorimeter we show an improved experimental setup combining the advantages of the different methods already described. Not only a high sensitivity in the pico Joule per Kelvin range is achieved but AC measurements at relative high frequencies are possible too. As another application the combination of both methods is possible where one can prevent crystallization by very fast cooling before following of the crystallization at temperatures below the maximum crystallization temperature using the AC measurement technique. The AC technique allows the investigation of crystallization at very slow rates not easy achievable by fast scanning also in thin films of semicrystalline polymers. Measurements on small samples of semicrystalline polymers are presented.

CPP 13.3 Tue 17:00 P3

The role of heat conducting walls in transient grating experiments — •Marianne Hartung and Werner Köhler — Physikalisches Institut, Universität Bayreuth

Laser-induced dynamic gratings are frequently employed for the measurement of heat conduction, Fickian diffusion and thermodiffusion in simple liquids and polymer solutions. We have analyzed experimentally and theoretically the systematic errors, which are caused by departures from one-dimensional heat conduction and diffusion. While the measured thermal diffusivities possibly have to be corrected for systematic errors, non one-dimensional mass diffusion has no effect on the experimentally determined mass and thermal diffusion coefficient.

M. Hartung, W. Köhler, Eur. Phys. J. E 17, 165 (2005)

CPP 13.4 Tue 17:00 P3

Ultra-fast scanning calorimetry of Poly(butylene terephtalate) — •Alexander Minakov[1,2] and Christoph Schick[2] — [1]Natural Science Research Center, A.M. Pokhorov General Physics Institute, Vavilov st. 38, 119991 Moscow, Russia — [2]University of Rostock, Department of Physics, Universitätsplatz 3, D-18051 Rostock, Germany

Ultra-fast scanning calorimetry (including controlled ultra-fast cooling) was applied to study crystallization and melting-reorganization processes in 40 ng Poly(butylenes terephtalate) (PBT) sample at the scanning rates up to 100000 K/s. We have found that the cold crystallization cannot be completely prevented in such sample even at the rates ca. 1000 K/s. The totally amorphous PBT sample can be obtained only at the rates ca. 10000 K/s. The melting-reorganization process was observed as follows. The sample was molted up to 350K with the rate 1000 K/s and cooled down to crystallization temperature with the same rate. The crystallization at 100 C, 130 C and 150 C was performed (3 min was enough for complete crystallization). Then the sample was cooled down to 24 C with the rate 1000 K/s. Next the melting-recrystallization curves were measured at the heating rates in the range 1000 - 40000 K/s. In the first case, the reorganization cannot be totally prevented even at 20000 K/s. We have found that few milliseconds were enough for recrystallization during fast heating after melting. In the sample crystallized at 130 C the recrystallization was prevented completely at the rate 10000 K/s, and at 5000 K/s in the sample crystallized at 150 C. We have found that 1 ms was not enough for reorganization in this case.

CPP 13.5 Tue 17:00 P3

Dynamic Structure Factor of Different Systems of Polymers — •Michael Strauch and Ekkehard Straube — Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik, Fachgruppe Theoretische Physik, Von-Seckendorff-Platz 1, D-06120 Halle (Saale)

In this poster we present our investigations concerning the dynamic structure factor $S_{\mathbf{q}}(t)$ in different systems of polymer chains.

In a first step, we have calculated the dynamic structure factor for a chain with randomly distributed friction coefficients ξ_i and spring constants k_i, thus generalising the result of the well-known Rouse model. In the more general case, the analysis can only be done numerically.

Furthermore, we have considered a network of polymer chains. In this case, one expects a finite value of $S_{\mathbf{q}}(t)$ for large times because the correlations between the chain segments do not completely vanish.

Finally, we compare our results with those of de Gennes where the chain dynamics are basically described as a purely longitudinal diffusion along the chain.

CPP 13.6 Tue 17:00 P3

New fast calorimeter for intermediate scanning rates — •Sergey Adamovsky and Christoph Schick — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18051 Rostock

For thermal measurements there are very sensitive differential scanning calorimeters available. The problem is that only relatively slow processes can be studied using a commercial device: heating rates of more than 300 K/min (5 K/s) are hardly reachable. On the other side, ultra-fast calorimetry was developed in the last years. These devices are suitable for very small samples and their heating rates only start at about 100K/s. So there was a gap from 5 K/s to 100 K/s. To cover this middle-range a new calorimeter was developed. The sensor is a 0.15 mm thick glass slide (a microscope cover slip was used); a Ni-heater and a Cu-Constantan (Type "T") thermocouple were deposited on the glass. The sensor is connected to a computer-controlled amplifier.

Application of the calorimeter for polymer materials is presented. Drying and solidification of modern paints as well as crystallization study of polymeric materials are presented.

CPP 13.7 Tue 17:00 P3

Pyroelectric tomography: Non-destructive 3D mapping of polarization profiles in poled polyvinylidene fluoride copolymer sensor cables — •Rosaura Flores Suárez, Michael Wegener, Werner Wirges, and Axel Mellinger — Department of Physics, University of Potsdam, Am Neuen Palais 10, 14469 Potsdam

The copolymers of polyvinylidenefluoride (PVDF) with trifluoroethylene are very attractive for sensor applications because they do not need to be stretched in order to become piezoelectric and may therefore be directly coated onto substrates or wires. P(VDF-TrFE) sensor cables may be used in such applications as traffic control or intruder monitoring in which their flexibility and rigidity as well as their rather high load tolerance are essential. In the present work, 3D polarization profiles in poled P(VDF-TrFE) sensor cables (diameter approx. 1.1 mm, thickness of the active layer approx. 200 μm) were measured by means of the focused thermal-pulse (TP) method [1] with a lateral resolution of 44 μm.

The relatively high data acquisition speed allowed the recording of up to 2 kPixels of in-plane data. The investigated sensor cables included samples poled with an industrial 4-needle corona setup, as well as samples poled under laboratory conditions using a single needle at voltages of -25 kV and -60 kV under different atmospheres (air and SF_6, respectively). By studying the polarization "footprints" of the corona needles. optimum poling geometries could be deduced.
[1] A. Mellinger, R. Singh, M. Wegener, W. Wirges, R Gerhard-Multhaupt and S. B. Lang, Appl. Phys. Lett. **86**, 082903 (2005).

CPP 13.8 Tue 17:00 P3

High NA UV digital in-line holography — •Martina Schürmann[1], Hans Jürgen Kreuzer[2], Michael Grunze[1], and Axel Rosenhahn[1] — [1]Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg — [2]Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia B3H 3/5, Canada

Holography is a lensless imaging technique with intrinsic three-dimensional properties. The radial divergence of spherical waves enables the acquisition of a magnified image of the sample. Unlike conventional microscopy, the method does not require lenses. The achievable resolution thus only depends on the wavelength of the light and the detection angle. With short wavelengths tiny objects can therefore easily be resolved. For the first time, UV laser light and a high numerical aperture setup were used in order to holographically enlarge transparent and opaque particles and characterize their imaging properties. Furthermore, fibroblast cells were imaged in order to explore future applications in biology. As the presence of the reference wave introduces the third dimension, first experiments demonstrating the three dimensional nature of the method are also shown. All results are compared to images obtained by conventional light microscopy.

CPP 13.9 Tue 17:00 P3

Imaging of surface and in depth modification of Polybutadiene (PBD) and silane-linked Polyethylenimine (PEI) films — •Martin Michelswirth[1], Thorsten Andres[1], Thorsten Meyer[2], Bernd Zimmermann[2], Manfred Neumann[2], and Ulrich Heinzmann[1] — [1]Molekül- und Oberflächenphysik, Fakultät für Physik, Universität Bielefeld — [2]Elektronenspektroskopie, Fachbereich Physik, Universität Osnabrück

We present the characterization of surface-structured thin Polybutadiene (PBD) and Polyethylenimine (PEI) films by Atomic Force Microscopy (AFM) and Imaging Ellipsometry. The surfaces of those 70 nm thin films were modified by a plasma modification process, using square meshes as "in contact masks". To investigate the resulting structures we performed AFM and Imaging Ellipsometry. In contrast to AFM, Imaging Ellipsometry enabled imaging of "in depth"modifications of our surface structures. Such "in depth"modifications were also investigated in branched and unbranched silane-linked organic layers of PEI. Additionally both the PBD and PEI films have been characterized by X-Ray Photoelectron Spectroscopy (XPS). The experimental results will be presented in detail.

CPP 13.10 Tue 17:00 P3

Torsional Quartz Crystal Resonators Contacting the Sample Face-On:Technical Aspects and Application to the Film Formation Process — •Alexander Martin König, Binyang Du, and Diethelm Johannsmann — Institute of Physical Chemistry, Clausthal University of Technology,Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld

Traditional AT-cut quartz crystal resonators operating in MHz range are extensively used to explore the interfacial properties of coatings. However, the penetration depth of the shear wave emanating from AT-cut resonators typically is hundreds of nanometers, limiting their applicability to thicker coatings. X-cut torsional resonator-operating in kHz rangeprovide for a complementary approach. Here, the penetration depth is hundreds of micrometers. We report on the use of torsional resonators only contacting the sample across the front face of the cylinder. As we show, the equations for the analysis of AT-cut resonator measurements can be used in the same way for torsional resonators operated in this mode. In particular, the experimental results show that the Sauerbrey equation also holds for torsional resonators. This finding turns them into suitable devices for investigating the film-formation process. By varying the concentration of the colloidal dispersions and controlling the evaporation rate of the solvent, different mechanisms of film-formation were observed. The mechanism of film formation can be inferred from the evolution of frequency and bandwidth as a function of time. The film is formed via wet-sintering for slow evaporation, while for fast evaporation the film is formed via dry-sintering.

CPP 13.11 Tue 17:00 P3

Spectroscopic Ellipsometric Light Scattering: a Tool for the Detection of Anisotropic Layers on the Interface of Colloidal Particles — •Arne Stark[1], Andreas Erbe[2] und Reinhard Sigel[1] — [1]Max-Planck-Institut of Colloids and Interfaces, D-14476 Golm — [2]University of Leeds, Leeds, UK

The sensitivity of ellipsometric light scattering (ELS) to anisotropy is demonstrated by model calculations and experiments on lipid vesicles. ELS is the combination of light scattering with the polarization optics and nulling scheme of an ellipsometer. Similar to reflection ellipsometry it is sensitive on interface layers, however not on flat interfaces but at the interface of colloidal particles to the surrounding solvent. The presented model calculations based on Mie theory indicate a change of the information content with varying wavelength. In addition, a strong effect of the layer anisotropy on the signal is found. Experiments on lipid vesicles confirm the significant effect of anisotropy. We were able to determine the optical anisotropy of these vesicles. From this, it is possible to estimate the average tilt angle of the lipid chain in the vesicle.

CPP 13.12 Tue 17:00 P3

Interfacial strength of the contacts between glass spheres and a solid surface investigated by torsional and thickness-shear quartz resonators — •Binyang Du, Alexander Martin König, and Diethelm Johannsmann — Institute of Physical Chemistry, Clausthal University of Technology,Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld

A torsional quartz resonator and a thickness-shear quartz resonator were used to study the interaction between a monolayer of glass spheres and the resonator surface. The glass sphere induces a negative or a positive frequency shift, depending on the mass of the sphere m_s, the spring constant of the sphere-plate contact, κ_s, and the frequency of the resonator ω. This behaviour can be explained by the "Mass-Spring-Model". [1] The sphere is considered as a second small resonator with a resonance frequency $\omega_s = (\kappa_s/m_s)^{1/2}$. For $\omega_s \gg \omega$, the spheres are rigidly attached to the crystal and behave like a Sauerbrey film. The frequency shift is negative. In the opposing limit of $\omega_s \ll \omega$, inertia holds the spheres in place. The sphere-plate contact increases the overall stiffness of the composite resonator and therefore increases the resonance frequency in proportion to the spring constant. Employing both thickness-shear resonators and torsional resonators and varying the sphere size, different regimes were mapped out. Interestingly, varying humidity of the environment changes κ_s as well as ω_s, leading to a cross-over from positive frequency shift to negative frequency shift. The results indicate that quartz resonators can probe interfacial capillary aging.
[1] G. L. Dybwad, Journal of Applied Physics 58, 2789 (1985)

CPP 13.13 Tue 17:00 P3

New methods for the characterisation of orientation in thin polymer films and application to light-induced anisotropy — •Christoph Jung[1], Joachim Stumpe[2], Olga Kulikovska[2], Emiel Peeters[3], and Bianca van der Zande[3] — [1]Lehrstuhl EPIV/ Prof. Dr. J. Köhler, University of Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany — [2]Fraunhoferinstitute of Applied Polymer Research, Geiselbergstr. 69, 14476 Potsdam, Germany — [3]Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

The recently developed method of Immersion Transmission Ellipsometry (ITE, patent pending) allows to fully characterise the absolute 3D refractive indices and the thicknesses of anisotropic films, which are thinner than the wavelength of the probing light, with high accuracy.The three-dimensional properties of anisotropic thin films are important for the display technology and optical data storage, predominantly. In addition, the method of waveguide spectroscopy is refined to explore the tilt gradient of thicker films in its profile. Different biaxial, tilted and splayed films were generated by photo-orientation and photoalignment in the bulk of photochromic and liquid crystalline polymer films and subsequently characterised.
[1] C. C. Jung and J. Stumpe; Immersion transmisssion ellipsometry (ITE): a new method for the precise determination of the 3D indicatrix of thin films, Appl. Phys. B, 80, 231-238 (2005).
[2] C. C. Jung, J. Stumpe, E. Peeters, B. M. I. van der Zande; Novel way for Full Characterisation of Splayed Retarders using Wentzel-Kramers-Brillouin Method, Jpn. J. Appl. Phys., 44, 4000-4005 (2005).

CPP 13.14 Tue 17:00 P3

In situ study on the mechanisms of living polymerization via small angle neutron scattering and 1H NMR — •Aizhen Niu[1], Joerg Stellbrink[1], Juergen Allgaier[1], Lutz willner[1], Dieter Richter[1], Bernd W. Koenig[2], Roland P. May[3], and L. J. Fetters[4] — [1]Institute fur Festkorperforschng, Forschungszentrum, Jülich GmbH, 52425 Jülich, Germany — [2]IBI-2, Forschungszentrum, Jülich GmbH, 52425 Jülich, Germany — [3]Institute Lau-Langevin, F-38042, Grenoble, Cedex 9, France — [4]School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14583-5201

In this work for the first time a combined 1H-NMR and small angle neutron scattering in situ study of the anionic polymerization was performed. Both initiation and propagation phases were explored. This combined technique allows the structural and kinetic characteristics to be accessed and cross compared. The smaller aggregates contain most of the reacted monomer. Their structure changes from high functionality wormlike chains at early stages of the reaction to star-like aggregates where the crossover occurs at a degree of polymerization of 40. It is clear that the measurement of kinetic orders is not a tool that can be used to assay aggregation states as has long been assumed. The period when initiation and propagation occurred simultaneously was found to consist of three regimes where the initiation rate increased with time, the aggregation states of the living chains are decreasing with increasing rate.