Coupling lab-based AFMs with ultrafast in-situ Nanocalorimetry in view of building a lab-on-a-chip platform for characterization of nanogram-sized samples

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Co-financing

18 months MSU + 18 months ESRF + 12 months MSU

Abstract

The proposed research program is methodologically focused on the in-situ combination of nano-calorimetry (NC) and atomic force microscopy (AFM) to enable simultaneous and quantitative determination of the surface features and thermal properties of a vast range of nano-sized and/or thin-film materials. The high heating and cooling rates (between 10^3 and 10^6 K/s) provided by the NC sensor based on micro-electro-mechanical-systems (MEMS), will for example allow unveiling the complex temperature-dependent micro/nano-structural evolutions occurring in semicrystalline polymers, as well as in polymer nanocomposites and thin films designed for organic photovoltaics applications. Importantly, the NC/AFM combination will enable quantitative investigation of multiple thermal transitions in nanogram-sized specimens, thus yielding information on e.g. the temperatures and enthalpies of the phase transitions, the degree of crystallinity, and the glass transition temperatures, which will enhance our understanding of the information delivered by simultaneous AFM imaging. The present project can be considered as a step forward with respect to the two LTP projects lead by the academic partner (SC-3457 and SC-3898). Complementarily to these LTPs focused on NC/X-ray combinations, this proposal aims at expanding significantly the performance of nano-calorimetry by coupling it with simultaneous AFM imaging using the lab-based commercial AFMs available at the PSCM. The methodological and scientific developments driven by this project will be beneficial for a broad scientific community working in the field of functional nanomaterials and polymer nanocomposites. The nano-calorimeter accessory for AFM, designed and realized by the academic partner, will be granted to the ESRF at the end of the project. We believe that this project will enhance the interest of a growing user community for in-situ combinations of novel emerging characterization techniques, thus contributing to the possible development of a future lab-on-a-chip platform.

Milestones

Year 1 (MSU-based):

Student training, development of new NC-sensors and first experiments at MSU.

Year 2 (6 months @ MSU + 6 months @ ESRF):

Transfer and adaptation of the NC sensors on PSCM AFMs

Year 3 (ESRF-based):

Combined NC/AFM experiments at the PSCM labs

Year 4 (MSU-based):

Publications, thesis defense, and first EBS-Era NC/X-ray experiments

1 Scientific background and motivation

Since the pioneering developments by Prof. L.H. Allen and coworkers [1], nano-calorimetry using miniaturized MEMS-based chips has proven to be a powerful technique for probing extremely small quantities of materials. This technique has been already applied successfully to the study of metals, nanoparticles, thin and ultra-thin films of amorphous and semicrystalline polymers, self-assembled monolayers, individual biological objects, and even explosives in trace amounts. It is noteworthy that the sensitivity of the calorimetric sensor can be pushed down to the nano-gram and even the pico-gram range thanks to the use of extremely fast cooling/heating rates (up to 10^6 K/s) that are completely inaccessible to conventional instruments such as the Differential Scanning Calorimeter (DSC). Nano-calorimetric applications are rapidly growing, and current bibliometric data demonstrate that this field is now entering the stage of exponential expansion. Nevertheless, nano-calorimetry should still be considered as a novel experimental method that has not yet reached the status of routine lab-based materials characterization technique. Further developments are needed, in particular to address the stringent requirements of a growing user community needing highly robust and reproducible quantitative results.

Growing market interest is demonstrated by the recent launching of the first commercial nano-calorimetry-based instrument ("Flash-DSC" by Mettler-Toledo). The peculiar design of this instrument however excludes any possible in-situ combination with other techniques. For this reason, the academic partner has developed during recent years custom-made devices allowing to respond to the ESRF user community's demand for combined nano-beam-X-ray-scattering/fast-calorimetry experiments (cf. the final report on LTP SC-3457, during which the first prototype nano-calorimetry accessories have been designed, built and commissioned for the ID13 beamline). Such experiments enable simultaneous determination of both thermo-physical and structural properties of nano-gram samples. It is noteworthy that the continuation LTP proposal SC3898 has been approved. This will allow synchronization with fast X-ray detection systems and with in-situ cryogenic chambers enabling nano-calorimetric experiments at low temperatures.

Synchrotron-based applications of nano-calorimetry are however only the most recent addition within an overall program that the academic partner initiated two decades ago. The initial methodological driving motivation for such a program was the combination of nano-calorimetry with commercial atomic force microscopes. This was pursued first at the Digital Instruments/Veeco Metrology Group [2] (Fig.1A), then at the Free University of Brussels [3-5] and more recently at CNRS-Mulhouse and Moscow State University [6] (Fig1B-D). The development of a nano-calorimetry/AFM platform for combined physico-chemical/morphological analysis of nano-objects and ultrathin films was awarded a prize by the Russian Government in 2013 [7, 8].

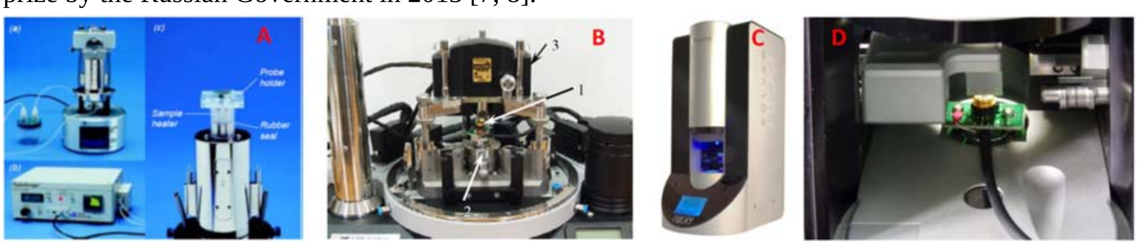

Figure 1 (A) The first-generation high-temperature AFM accessory developed with participation of the PSCM academic partner at Digital Instruments (USA) [1]: (a) MultiMode microscope head with the thermal accessory installed; (b) temperature controller; (c) main components of the thermal accessory assembled on the piezo-scanner. (B) General view of a combined system INTEGRA-AFM/Nanocalorimeter developed at MSU: 1 – Nanocalorimeter sensor holder, 2 – INTEGRA stage, 3 – measuring head. (C) View of the C3M SOLVER NEXT AFM available at MSU. (D) Combination of the C3M AFM with the Nanocalorimeter performed at MSU.

The methodological advances proposed in this project are of interest not only for academia but also for private companies involved in the development of scientific instrumentation (e.g. NTMDT, Russia), as well as in the production of commodity semicrystalline polymers (e.g. Dow Chemical, DSM, Solvay). The targeted combination of quantitative thermal analysis and surface-sensitive AFM techniques will enable enhanced understanding of the microstructural evolution in complex soft-matter systems. The new experimental techniques and scientific results generated within the framework of this project will attract new academic and industrial collaborations for the PSCM in particular and the ESRF in general.

2 Scientific goals and technical approach

Among the many possible scientific targets, we concentrate on three case-studies: (a) crystallization and melting of semi-rigid poly(trimethylene terephtalate) (PTT) and similar semicrystalline polymers (PET, PLLA); (b) thermal and structural response of thin-film polymer blends (P3HT/PCBM and PTQ/PNDIT) for applications in organic photovoltaics; (c) phase behavior and microstructure of thin polymer nanocomposite films (poly(p-xylylene)-silver) prepared by low-temperature vapor deposition polymerization. An example of a typical temperature-resolved AFM image sequence is presented in Fig. 2. Additional information on the systems studied and the scientific goals is provided in the annex.

Further development of MEMS-based ultrafast calorimetry coupled to AFMs will lead to a PSCM experimental platform for combined physico-chemical characterization of nanogram-sized samples. This will be achieved via the know-how developed at MSU for the integration of nanocalorimetry with the AFMs INTEGRA (Fig. 1B) and C3M SPM SOLVER NEXT (Fig. 1C-D). These instruments significantly expand the possibilities of scanning probe microscopy in terms of analysis of topography and surface properties of thin films and nano-objects used in functional nanomaterials. This enables quantitative correlations between the samples' structural and thermal properties, which is extremely useful for example in the study of thin-film devices for organic electronics. For such devices, it is important not only to control the conditions of their preparation, but also to monitor their microstructural evolution during operation. The Nanocalorimeter accessory facilitates such investigations via easily programmable fast heating/cooling cycles coupled with online AFM imaging. In the C3M system in particular, the movement of the laser and photodiode is fully automated using stepper motors. An original algorithm allows adjusting the position of the laser and photodiode automatically, executing the whole alignment procedure in 10-20 seconds. The low noise characteristics of this instrument allow spatial resolutions down to the atomic scale, while working both in STM and AFM modes. We will transfer the MSU know-how and design/produce/install new nanocalorimeter units for the PSCM AFMs in order to achieve also at the ESRF the best possible coupled AFM/NC performances.

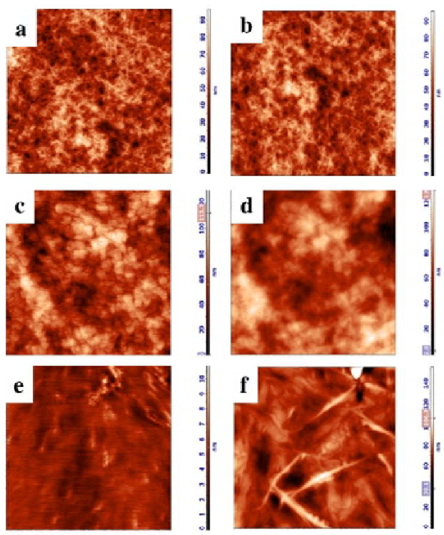

Figure 2 *Temperature-dependent surface topography of a sPP/PEO thin film monitored with the INTEGRA-AFM/NC system. Image size is 5 μm and the height scale is reported at the right side of each panel. (a) 25 °C, (b) 60 °C, (c) 80 °C, (d)110 °C, (e) 130 °C, (f) 60 °C.*

During the first 18 months, the student will be based at MSU to develop the first two experimental programs listed above. This will be done using the INTEGRA-AFM/NC (Fig. 1B) and C3M-AFM/NC (Fig.1 C-D) systems developed at MSU. In parallel with this activity, the details of the lab-based PSCM commercial AFMs will be acquired to design and produce new custom nano-calorimeter sensors. During the subsequent 18 months the student will be based at the PSCM to transfer, test and integrate the new sensors. Reproducibility studies for projects (a) and (b) will enable a thorough assessment of the functionality of the AFM/NC implementations at the PSCM. Extension to project (c) will produce genuinely new results at the PSCM, to be subsequently confirmed at MSU. In parallel with this activity, the student will participate in beamtimes at ID13 acquired via standard or LTP proposals. The student will spend the 4^{th} year back at MSU to finalize data analysis, publications and thesis defense. Optional visits at the ESRF as standard user after EBS startup may facilitate the definition of a subsequent phase for this collaboration.

3 Time schedule with milestones

Year 1 (October 1, 2016 - September 30, 2017: PhD student based at Moscow State University)

- Thorough PhD student training in AFM, X-ray scattering and Nanocalorimetry;
- Design and realization of a nanocalorimetric sensor holder compatible with the AFM sample environments;
- First tests of the AFM/Nanocalorimeter combination on systems comprising semicrystalline polymers such as PET, PTT, PLLA.

Year 2 (October 1st, 2017 - March 31, 2018: student based at MSU; April 1st, 2018 - September 30, 2018: student based at the ESRF)

- Extension of the combined AFM/Nanocalorimeter studies on the active layers of organic photovoltaics (e.g., P3HT/PCBM and PTQ/PNDIT systems);
- First experiments at the ESRF to check and improve the compatibility of the developed nanocalorimetric accessory with the AFMs present at the PSCM labs;
- Complementary experiments using a combination of nanobeam X-ray scattering and nanocalorimetry at the ID13 beamline (via beamtime proposal applications).

Year 3 (October 1st, 2018 - September 30, 2019: student based at the ESRF)

- Combined AFM/Nanocalorimeter studies on thin polymer nanocomposites films including poly(p-xylylene) – silver prepared by low-temperature vapor deposition polymerization;
- Studies with a combination of nanobeam Grazing-Incidence X-ray diffraction and Nanocalorimetry at the ID13 beamline before the long shutdown;
- Dissemination to conferences and scientific publications.

Year 4 (October 1st, 2019 - September 30, 2020: student based at the MSU)

- Dissemination to conferences and scientific publications;
- First EBS-era experiments using a combination of nanobeam X-ray scattering and nanocalorimetry at the ID13 beamline (via standard proposal applications);
- Submission of dissertation and thesis defense.

4 Additional information

We propose this project as a co-funded PhD program involving a student enrolled at Moscow State University for a total of 48 months. The student will spend a continuous period of 18 months (April 1st, 2018 - September 30, 2019) at the ESRF in PSCM premises. The student will be supported by ESRF funds during the stay in France, and by the Russian state PhD bursary and Russian research grants during the rest of the PhD program. PhD students in Russia are selected based on the results of an entrance examination performed in September. We have several promising candidates but we cannot already name a specific student at this early stage. The starting date of PhD programs is not flexible in Russia, and is fixed to be October 1st, 2016.

The main outcome of this project for the ESRF will be the design and realization of a nanocalorimeter accessory compatible with the commercial AFM instruments available at the PSCM labs. The Nanocalorimeter and the calorimetric measuring cell for the AFMs will be built at MSU and delivered to the ESRF. The accessory, as well as the stand-alone Nanocalorimeter, will stay at the ESRF and will be accessible to all interested users.

[1] S. L. Lai et al, *Physical Review Letters 77* (**1996**) 99-102. [2] "Exploring the High-Temperature AFM and Its Use for Studies of Polymers" D.A. Ivanov; R. Daniels; S. Magonov, Application Note published by Digital Instruments/Veeco Metrology Group (**2001**). [3] C. Basire; D.A. Ivanov, *Physical Review Letters 85* (**2000**) 5587-5590. [4] D.A. Ivanov; Z. Amalou; S.N. Magonov, *Macromolecules 34* (**2001**) 8944-8952. [5] S.N. Magonov; N.A. Yerina; G. Ungar; D.H. Reneker; D.A. Ivanov, *Macromolecules 36* (**2003**) 5637-5649. [6] D.A. Ivanov et al, *Macromolecules 41* (**2008**) 9224-9233. [7] http://www.rg.ru/2014/02/12/premia-dok.html [8] http://www.physchem.msu.ru/labivanov.html

Annex to PhD proposal

Coupling AFM with ultrafast in-situ Nanocalorimetry in view of building a lab-on-a-chip platform for characterization of nanogram-sized samples

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Additional information on scientific goals, samples studied, and technical motivations.

In the present project, the versatility of the in-situ combination of nanocalorimetry and AFM will be shown using three different classes of soft-matter systems. In the frame of the first class, i.e. **semicrystalline polymers**, the research will benefit from the experience of the academic partner in applications of high-temperature AFM acquired over many years [3-5]. The proposed studies will improve our understanding of the structure formation and reorganization processes operating in semicrystalline polymers. In particular, the in-situ nanocalorimetric accessory to be developed in the project will greatly enhance the time resolution of high-temperature AFM, which was missing before. Thus, the high heating rates provided by the nanocalorimetric sensor, will allow performing short-term annealing of the sample at elevated temperatures followed by virtually instantaneous cooling of the sample down to the ambient or, more generally, imaging temperature. Thus, a semicrystalline polymer sample placed in the AFM can be subject to dwellings at elevated temperatures for the times as short as 1 millisecond, which is a typical time response of the sensor itself. By performing repetitive short-term annealings followed by imaging at a lower temperature, one can get insights in the mechanisms of the high-rate reorganization processes operating in semicrystalline polymers. Despite extensive studies performed in the past, the exact nature of such reorganization processes constitutes a long-standing issue in polymer physics. It is well documented that many semicrystalline polymers demonstrate a very complex thermal behavior [e.g., 6]. For these materials, even isothermally crystallized samples can exhibit several melting endotherms in the DSC heating traces [e.g., 7]. It is important to stress that the multiple melting behavior cannot be accounted for by the presence of different crystalline polymorphs as it is observed also for polymers exhibiting only one crystalline modification. Understanding of the mechanisms of polymer microstructural reorganization during thermal treatments is of paramount importance not only for academic research but also for numerous practical applications of such commodity polymers produced at the scale of many millions of tons per year. In the frame of the proposed PhD studies, the structure formation and reorganization processes will be addressed for two typical aromatic polyesters, PET and PTT, which are significantly different with respect to the chain conformation in the unit cell, as well as for one representative biodegradable aliphatic polyester, PLLA.

The second class of systems to be tackled in the project will be **organic solar cells**, which are based on a novel technology exploiting organic semi-conducting materials for conversion of solar light into electricity. Although external quantum efficiency (EQE) of the devices, based on silicon, is much higher than that of the organic solar cells, the conjugated organic materials have very high coefficients of absorption. This fact allows producing devices with active layer thickness in the submicron range. Such organic materials may be deposited on flexible substrates using a continuous process at room temperature that allows reaching a very high production and low costs. The organic solar cells have a clear potential as a cheap renewable power source for realization of the so-called "green energy" concept. The combination of thermal properties and morphology of the active layers of organic solar cells (i.e. for films of 50-100 nm thickness) will be studied for the by now traditional system, i.e. P3HT/PCBM, in which the electron acceptor is a fullerene derivative. However, in addition, we will explore novel all-polymer solar cells (e.g., PTQ/PNDIT), in which semiconducting polymers are used as both electron-donors and – acceptors. The semiconductors will be synthesized by the group of Dr. A. Kiriy at Leibniz Institute for Polymer Research (Dresden). This subclass of solar cells is a viable alternative to fullerene-based polymer solar cells because of higher efficiency of light collection by semiconducting polymers, better optimized energy levels of donor and acceptor, better processability and environmental-friendly way of production [8]. However at present, most of the known all-polymer solar cells suffer from low EQE, related to improper blend morphology and interface structure, which are the cause of efficient geminate or non-geminate recombination. Therefore, one of the ways to improve effectiveness of the all-polymer solar cells is to optimize their morphology and the structure of the donor-acceptor interface. This task clearly requires morphological investigation such the one that can be provided by variable-temperature AFM imaging.

The third class of systems to be investigated in the project will comprise thin **polymer nanocomposite films**. In particular, the research will be focused on composites with silver nanoparticles embedded in a polymer matrix, which are the subject of substantial interest of physicists, chemists, material scientists and biologists due to their novel optical properties. The potential application fields of these materials include fabrication of miniaturized optical devices for chemical and biological sensing and imaging, surface-enhanced Raman and infrared spectroscopy, plasmon-enhanced fluorescence and others [9]. The functional properties of these materials are mainly connected to surface plasmons, which are coherent oscillations of conduction electrons excited by electromagnetic radiation at the metal/dielectric interface. Among the three metals (Ag, Au, Cu) that can exhibit surface plasmon resonance in the visible wavelength range, silver has the highest efficiency of plasmon excitation. The optical response of metal nanoparticles can be tuned by controlling their size, shape and local dielectric environment. The access to highly time-resolved imaging will help us to better understand the temperature-induced phase transitions of the polymer matrix (poly(p-xylylene)) and those of the nanoparticles that were recently the object of our preliminary investigation [10].

As far as the technical aspects and challenges of the studies are concerned, it is worth mentioning that the laboratory of the academic partner at the Moscow State University [11] has recently started efforts to compatibilize the nanocalorimetric accessory with AFM setups. Thus, in collaboration with the first Russian producer of AFMs, NTMDT company at Zelenograd, close to Moscow, the laboratory has developed two combined setups with the Nanocalorimeter installed on INTEGRA AFM (cf. Fig. 1) and C3M SOLVER NEXT AFM (cf. Fig. 2). The imaging tests verified that the intermittent contact scanning remains stable and the quality of the images has not been compromised. For the development of the Nanocalorimeter as a platform for combined physical-chemical analysis of nano-objects and ultrathin films, the academic partner of the project received a prize of the Russian government in 2013 [12].

[1] Allen, L. H.; Ramanath, G.; Lai, S. L.; Ma, Z.; Lee, S.; Allman, D. D. J.; Fuchs, K. P. *Appl. Phys. Lett.* **1994**, *64*, 417. [2] "Exploring the High-Temperature AFM and Its Use for Studies of Polymers" D.A. Ivanov; R. Daniels; S. Magonov, Application Note published by Digital Instruments/Veeco Metrology Group (**2001**). [3] C. Basire; D.A. Ivanov, *Physical Review Letters 85* (**2000**) 5587. [4] D.A. Ivanov; Z. Amalou; S.N. Magonov, *Macromolecules 34* (**2001**) 8944. [5] S.N. Magonov; N.A. Yerina; G. Ungar; D.H. Reneker; D.A. Ivanov, *Macromolecules 36* (**2003**) 5637. [6] G. Qiu, Z.-L. Tang, N.-X. Huang, L. Gerking, *J. Appl. Polym. Sci. 69* (**1998**) 729. [7] Z.-G. Wand, S. Hsiao, B. Sauer, W. G. Kampert, *Polymer 40* (**1999**) 4615. [8] C. R. McNeill and N. C. Greenham, Conjugated polymer blends for optoelectronics, *Adv. Mater. 21* (**2011**) 3840. [9] N. J. Halas, S. Lal, W.-S. Chang, S. Link, P. Nordlander, *Chem. Rev. 111* (**2011**) 3913. [10] D.R. Streltsov, K.A. Mailyan, A.V. Gusev, I.A. Ryzhikov, Y.I. Kiryukhin, A.S. Orekhov, A.L. Vasiliev, N.A. Erinad, A.V. Pebalk, Y.I. Odarchenko, S.N. Chvalun, and D.A. Ivanov *Polymer 71* (**2015**) 60. [11] http://www.physchem.msu.ru/labivanov.html [12] http://www.rg.ru/2014/02/12/premia-dok.html