Project Description – Project Proposals

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Photoswitchable surface topographies based on responsive hydrogels with embossed surface nanostructure for the systematic investigation of wetting dynamics

Project Description

### 1   State of the art and preliminary work

Switching of surface topography and responsive hydrogels

Many different concepts for the alteration of a surface topography exist, including the use of shape memory polymers[1,2], magnetic fluids[3,4], hydrogels[5–7] and liquid crystals[8,9] (Figure 1). Most of them, however, come along with a change of additional surface parameters. Shape memory polymers for instance, normally used to form switchable nanoscopic features on a respective surface, change the degree of crystallinity upon the transition thereby also changing their specific surface energy. So do liquid crystal systems. Responsive hydrogels as topography changing entity are adopting a different hydrophilicity upon the transition. The same is true for mixed polymer or block copolymer brushes[10], whose different components will stretch away from the surface one at the time at specific conditions. There are contributions dealing with ferrofluids that show a response when being exposed to a magnetic field. One could argue that the response of the ferrofluid does indeed only change the shape and no other parameter of the material. However, often these fluids are used in combination with other material, as it is the case for instance for a ferrofluid infiltrating a microstructured matrix.[4] Here, the response leads to a different degree of surface exposure of the microsized features on the surface, thus again changing the actual chemical composition of the surface upon the transition. The concept of stretching wrinkled PDMS based surfaces in order to diminish the wrinkle features, as an example for a topography change without alteration of other surface parameters, has been established already.[11–13]   However, in some of these cases, the focus was put on tunable adhesion and not on wetting and in all cases the stretching occurred manually by applying mechanical force to the substrates. An optical trigger has not been used yet with stretchable, wrinkled surfaces, thus, a fast, externally triggered and spatially resolved response is not yet available for these systems.

Optical triggers have been used already for surface topography changes, however, not to a large extent. One specific example is the use of a spiropyrane based gel. Spiropyrane ionizes upon UV-impact. Consequently, spiropyrane containing gels will strongly hydrophilize and in turn swell when going through the photo-triggered transition. Another way to induce a strong response in a gel by a light trigger is to use photosensitive crosslinks. These are mostly based on hoest-guest complexes involving cyclodextrine (CD) as a hoest and a photoswitchable azobenzene derivative as a guest[14,15] (see subsection "azobenzene chemistry"). The trans-cis transition of the azobenzene moiety leads to a reversible breakup of the crosslink forming complexes with the cyclodextrine. Thus, a strong increase in the swelling degree of the gels occurs. The breakup of the photolabile Azo/CD linkage is reversible, however, the re-formation of these linkages will not induce deswelling of the gel into the original state, as a respective force triggering the gel collapse is then absent. Yet, a strong, reversible response involving azobenzene is still possible if the photosensitive group is combined with a thermosensitive gel matrix. The polarity change of the azobenzene moieties upon the phototrigger is changing the

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lower critical solution temperature of the thermosensitive polymer backbone.[16] If the temperature is set close to the volume phase transition point of the gel, exposure to light can induce a strong alteration in the swelling degree of the gel.
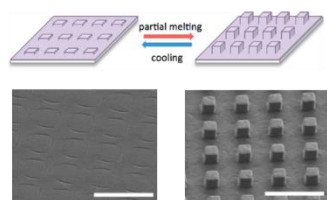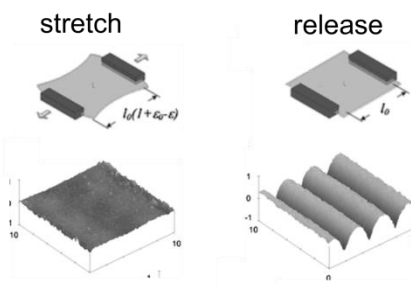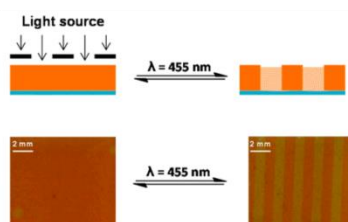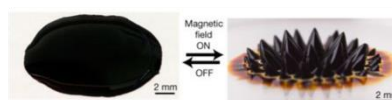

Figure 1. A selection of concepts for a switchable surface topography.[1,4,5,11]

A common problem with responsive gels is the retardation of the response caused by diffusional limitations and an insufficient penetration of the light into the bulk of the gel. One way to address this problem is to limit the spatial dimensions of the gel. Mourran et al. showed how hydrogels can be addressed by light with a very fast response.[17] The gels were thermosensitive and at the same time loaded with gold nanorods that generate the heat upon irradiation with light. The dimensions of the gels were kept in the micrometer range, so that no retardation in the gel swelling/deswelling occurred. In fact, the response was so fast, that the gels could follow a sound wave modulated light signal in realtime. These microgels were referred to as "dancing" microgels.

Azobenzene / arylazopyrazol chemistry

Azobenzene derivatives constitute one of the most widely used structural motifs in light responsive polymers and materials.[18,19] The metastable cis-form of the azobenzene basic unit can be transformed into the thermodynamically stable trans-form and vice versa by illumination with light of different wavelengths (Scheme 1A). As the two forms exhibit different polarity, the transition from one isomer to the other induces a polarity change on respective azobenzene containing materials, hence the light responsiveness. As the change in polarity is rather weak, azobenzene is often used in more complex structures that are supposed to strengthen the effect. Azobenzene as a crosslinking bridge for instance would induce strong material deformation upon the transition.[20] The co-presence of azobenzene and α- or β-cyclodextrine on the other hand opens a route towards photolabile linkages. Here, the trans-form of azobenzene can form an inclusion complex with the cyclodextrine moiety while the cis-form is not capable of doing that. Hence, a breakup of the crosslinks occurs upon illumination.[14,15] Ravoo et al. showed that the light induced switchability is stable over several cycles.[21,22] As mentioned in the previous subsection, the polarity change of an azobenzene derivative can be coupled to a thermoresponsive polymer matrix, rendering the LCST of the latter photosensitive. This example constitutes another possibility of strengthening the effect of the photoswitch of azobenzene.

A)

B)
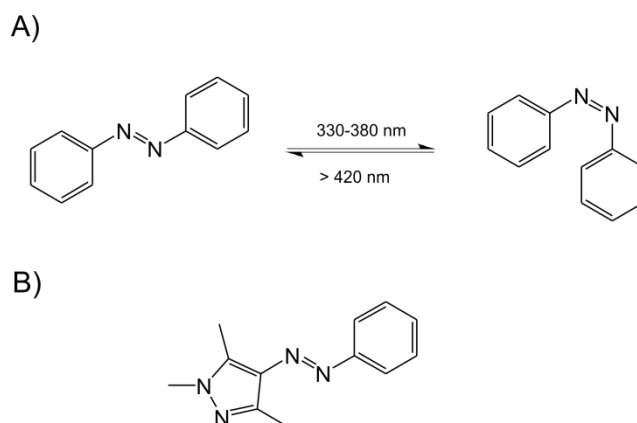
Scheme 1. A) Photoswitch based on azobenzene structures. UV-light triggers the trans-cis-isomerization causing a polarity change, while visible light in the blue range triggers the inverse reaction. B) Structure of arylazopyrazol, a very effective photoisomerizable group from the azobenzene family.

Despite its frequent use, azobenzene as a photoswitchable group comes along with a number of disadvantages including the low wavelength needed for the transition from trans to cis but most of all the low yield of the isomerization reaction. This is rather unfortunate as a proper macroscopic response is only ensured, if the isomerization of Azo is more or less complete. Hence, many researchers have tried to optimize the photoswitching properties of azobenzene with respect to transition wavelength and yield, for instance by a partial substitution[23] on or within the central azobenzene motif or by multimerization of the latter.[24] Recently, arylazopyrazole has been introduced (Scheme 1B)[25], a particular representative of a class of improved azobenzene based structural motifs in which one benzene ring is substituted by an aromatic heterocycle. These compounds show complete photoisomerization in both directions and very long half-lives of the cis isomer. Thus, an effective switching is ensured. Ravoo et al. have recently contributed a lot of work on light-responsive systems with improved photocontrol relying on arylazopyrazoles as the basis for these systems.[26] In a recent publication, AAPs with different substitution patterns were thoroughly investigated[27] and important conclusions were drawn with respect to the optimum strategy for an effective switching.

Dynamic wetting on (photo-)switchable substrates

Switchable substrates have already been utilized for the investigation of wetting processes for quite some time. The motivation behind most of these investigations was to explore proper conditions for a number of applications including controlled drug delivery, microfluidic channels, sensors and many more.[28–32] The underlying switching mechanisms for such investigations typically rely on reversible changes in the surface chemical composition and/or surface topography while applied triggers include pH-changes, temperature, light, electric fields and others.[33] A particular focus is put on light as a trigger, as this means easy operation and limited environmental impact.[33] UV-responsive inorganic materials like ZnO_2 or TiO_2 that change their wettability upon irradiation, are cheap and easy to implement. The reversibility however occurs only on a rather long time scale, as the switch back to the original surface properties occurs only by storage in the dark for a prolonged time. Much more sophisticated are organic materials, as they are constituted by a great variety of functional groups and molecular architectures. Consequently, the creation of custom-made photoswitchable surfaces and in turn the tuning of a respective response is easily possible. One of the most prominent examples for an organic, photoswitchable structure is the previously mentioned azobenzene (and its derivatives). A general problem with photoresponsive surfaces based on organic materials is the relatively small change in wettability upon the transition, meaning that a switch between two extreme wetting states is difficult to achieve. One particular contribution was given by Groten et al. were a fluorinated azobenzene moiety in combination with a nanoscale surface roughness was used to switch wettability between a Wenzel state and a superhydrophobic or a superwetting state.[34] This work showed that response amplitudes can be strongly enhanced when the photochemistry is done on rough surfaces. However, the interplay between surface roughness

and wettability changes upon surface chemistry change is still not well understood. Sometimes, large changes are observed, while in other cases differences are small.

On top of that, most case studies involving switchable substrates focused on static wetting characteristics rather than the dynamics. This is an issue, given the fact that often contact angle hysteresis occurs which means that the measured static contact angle is only an intermediate value between two extreme cases, the so-called advancing contact angle and the receding contact angle.[35] The occurrence of the hysteresis is a result of surface heterogeneities or surface forces acting in the vicinity of the contact line. Advancing and receding contact angle can only be measured, when the contact line moves, i.e. they can be measured only under dynamic conditions. In one of the few contributions with dynamic wetting as research subject, Mele et al. utilized a nanostructured, spiropyrane functionalized surface[36] to study the influence of the periodicity of the nanofeatures on the wetting dynamics. Controlled and repeated photoswitching of the surface chemistry allowed for precise monitoring of contact angle evolution. The authors could also demonstrate the reversibility of the wetting process over a course of at least 3 cycles. In another contribution, mechanical stretching of a wrinkled surface was used to investigate the contact angle anisotropy on a surface with uniaxially oriented nanofeatures[12] and the inversion of this anisotropy upon the stretching step. The influence of the hardness of the surface and the presence of surface cracks were investigated with the conclusion that a soft, crack free surface is superior in enabling a switchable anisotropic wetting that can be run over several hundred cycles without performance loss.

Liquid movement on surfaces triggered by gradients

Gradient substrates are substrates that change their chemical or physical properties in a continuous manner across their surface. As these properties strongly influence the wettability, these gradients may be the basis for directed motion of liquids along the surface. As a liquid droplet on a surface has a certain spatial extent, the presence of a gradient along the surface and thus along the droplet extent causes an imbalance of surface tension forces acting on the droplet. Consequently, the droplet moves, even against gravitational forces. One of the first examples for using a chemical gradient to make a droplet move was demonstrated by Chaudhury and Whitesides in 1992.[37] Here, a hydrophobicity gradient was implemented on a surface originating from an exposure of the latter to decyltrichlorosilane vapor. In another contribution, a chemical gradient was introduced by adjustment of the hydrolyzation time of a polyanhydride covered surface.[38] A chemical gradient originating from the nanopatterning of a SiO_2-surface was used by Bliznyuk et al. (Figure 2A).[39] Here, it was the periodicity of the nanosized hydrophobic features on the hydrophilic SiO_2-surface that gradually changed along the substrate surface. A pure shape gradient was applied by Zhang et al.[40] Here, a specifically shaped hydrophilic mica specimen was pressed into the surface of a hydrophobic, soft substrate composed of wax or LDPE. The mica area was shaped as a thin stripe whose width gradually changed along the stripe axis (Figure 2B). Along this axis, the liquid could move. A concept of using a gradient in the periodicity of a wrinkled surface for self-propelled particle motion has been demonstrated in our group (Figure 3).[41] The motion originated from different contact angles at different lateral positions on the wrinkled surface that where the result of a changing wrinkle wavelength an amplitude across the substrate surface.

All the presented examples represent systems, in which the gradient is embossed into the surface layer without the opportunity to change it at a later stage by applying an external trigger. However, spatial gradients can also be induced on demand and in a time resolved manner. One example is based on the use of electroactive surfactants where droplet movement is triggered by an electric field.[42] As surface tension is depending on temperature, a simple thermal trigger can be applied as well.[43–46] In one contribution for instance long-chain alkanes close to their melting point were used.[47] Often, the external switch can be applied in both directions thus rendering the movement reversible. An optical trigger for the induction liquid motion has been frequently reported.[48] Yet again, the reported systems show surface changes that are not exclusively based on topography changes but also involve the change of the surface chemistry.
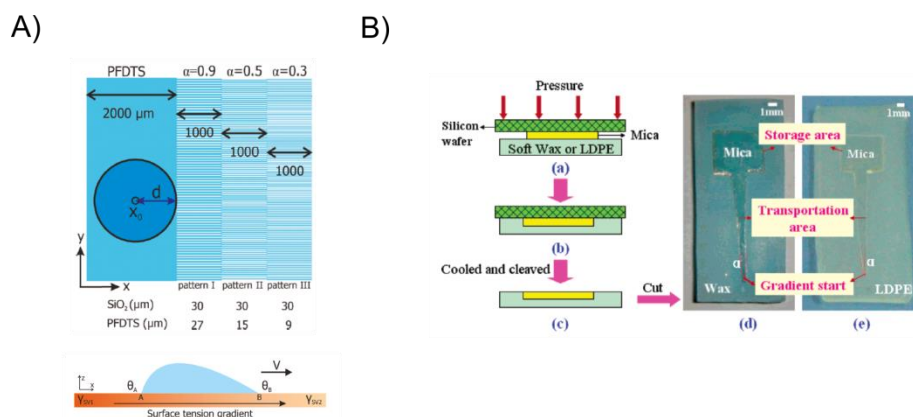
Figure 2. Different concepts for liquid movement on gradient surfaces: A) chemical gradient based on a changing periodicity of nanosized, hydrophobic SiO_2-based features B) a specifically shaped hydrophilic mica area embossed into a hydrophobic, soft material (wax or LDPE);.[39,40]
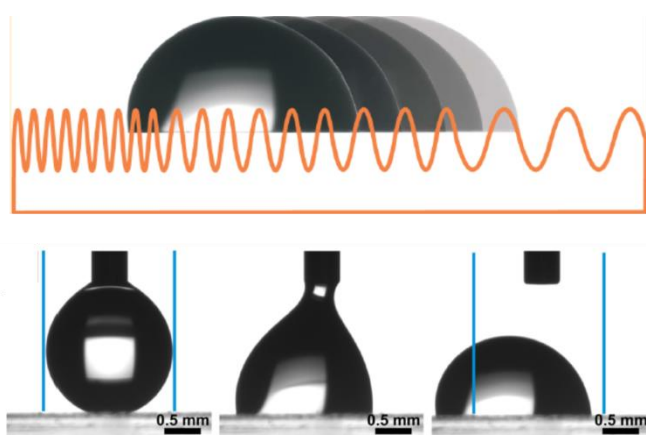

Figure 3. A periodicity gradient in the nanofeatures of an uniaxially wrinkled surface inducing droplet movement.[41]

Most studies of self-propelled or externally triggered droplet motion have specific applications in mind. If it is possible to induce directed droplet movement, microfluidic devices are thinkable that work without walls or channels.

Preliminary work

The controlled wrinkling of the surfaces of PDMS-based substrates by application of mechanical stress in combination with plasma treatment is a technique on which we have gained a lot of experience in the last years. We have investigated basic parameters of the process in order to fully understand the underlying mechanism[49, A1] and to control the size and shape of the surface pattern to be generated[49, A1] (see Figure 5 and 6) and also screened and assessed respective data from literature in a review.[50] We used the wrinkling process to generate masters for microcontact printing in order to provide a method for the large-scale generation of nanostructured polymeric surfaces[51] and for the generation of anisotropic patches on microparticles.[52] The replication of the wrinkle features into very different kinds of materials including polymers and ceramics[53] has been demonstrated, and last but not least, we have shown how the wrinkled structures can be used as template for particle alignment.[54–56] Special emphasis is put on a work by Wünnemann et al. from 2016 in which we demonstrated the possibility to replicate the wrinkle nanopattern into a hydrogel surface (Figure 4).[57,A2] In an unpublished work, we could also show, how to create a more complex radially symmetric wrinkle pattern that could also find application in the current proposal.
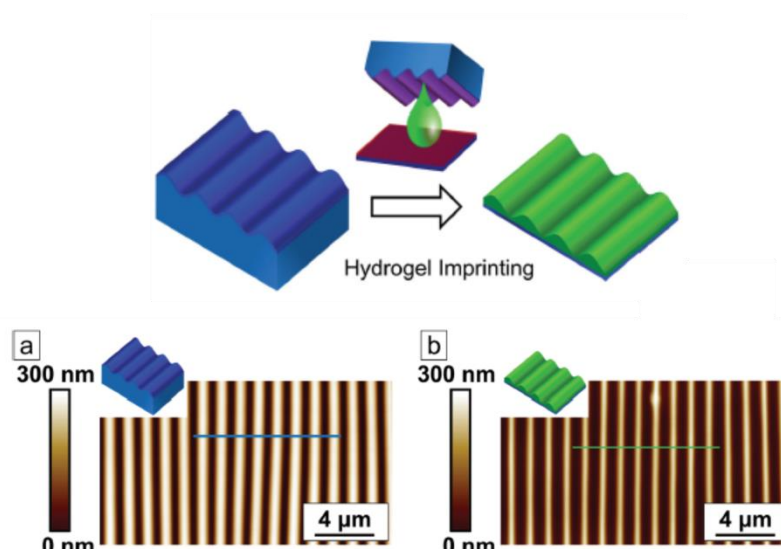
Figure 4. Replication of a wrinkle pattern on a PDMS substrate into the surface of a hydrogel specimen.[57]

Using wrinkled surface structures for the induced movement of liquid droplets was demonstrated by us in 2016 (Figure 3).[41, A3] Here, we forced a periodicity gradient into the wrinkle structure which lead to asymmetric wetting and in turn the movement of a deposited droplet.

Azobenzene chemistry has been used by us to generate light-responsive hydrogels[58, A4], while also other concepts of light triggered hydrogel transitions have been followed.[59] Additionally, there is experience in the project group on the synthesis of functional, responsive hydrogels and polymers.[16,58, A5] The latter will be useful for the synthesis of the photoresponsive hydrogels exhibiting tailored properties that fit our needs for the dynamic wetting studies.

1.1   Project-related publications

1.1.1   Articles published by outlets with scientific quality assurance, book publications, and works accepted for publication but not yet published.

A1) Hiltl, S.. " Wrinkle-Assisted Particle Assembly and Design", Dissertation, Aachen, **2015**.

A2) Wünnemann, P.; Noyong M.; Kreuels, K.; Brüx, R.; Gordiichuk, P.; van Rijn, P.; Plamper, F. A.; Simon, U.; **Böker, A.** "Microstructured Hydrogel Templates for the Formation of Conductive Gold Nanowire Arrays" *Macromol. Rapid Commun.*, **2016,** *37*, 1446-1452.

A3) Hiltl, S.; **Böker, A.** "Wetting Phenomena on (Gradient) Wrinkle Substrates" *Langmuir*, **2016**, *32*, 8882-8888.

A4) **Reinicke, S**.; Espeel, P.; Stamenović, M. M.; Du Prez, F. E. "Synthesis of multi-functionalized hydrogels by a thiolactone-based synthetic protocol" *Polym. Chem.* **2014**, 5, 5461-5470.

A5) **Reinicke, S.**; Espeel, P.; Stamenović, M. M.; Du Prez, F. E. "One-Pot Double Modification of p(NIPAAm): A Tool for Designing Tailor-Made Multiresponsive Polymers" *ACS Macro Lett.*, **2013**, *2*, 539-543.

1.1.2   Other publications

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1.1.3   Patents

1.1.3.1   Pending

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1.1.3.2 Issued

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2   Objectives and work programme

2.1   Anticipated total duration of the project

36 months

2.2   Objectives

The main project goal is to develop a new concept for a switchable surface in which only the surface topography and no other parameter changes upon an external trigger while a fast and reversible response is ensured. The trigger of choice is light due to its easy implementation, low environmental impact and high spatial and temporal control. The material basis for our concept is a thermo- and photosensitive hydrogel stripe onto which specific surface topographies are impregnated and which is covered with a non-responsive, but ultrathin top layer that prevents the surface from changing its hydrophilicity upon the phototriggered transition. With the established concept we want to perform case studies for the investigation of dynamic wetting phenomena, given the fact that research involving switchable surfaces so far has mostly focused on static wetting. Having in mind the strong influence of surface roughness on the wettability of surfaces, the response is designed in a way that switching between extreme wetting cases can occur (see concept). Repeated switching in a periodic manner will give us the opportunity to study the coupling of the wetting dynamics to the surface response on a fast time scale. Variation of the basic surface topography as well as of surface chemistry will provide us the opportunity to address different fundamental wetting cases in order to show the broad applicability of the concept. In addition to the dynamic wetting investigations, the use of topography-switchable surfaces with different chemistry will also allow to gain a better understanding on how surface roughness is enhancing wettability differences for changing surface chemistries. Finally, by using time and space resolved illumination, using a moving mask, a new concept for droplet movement on a planar surface will be demonstrated.

2.3   Work programme incl. proposed research methods

Concept:

The general concept for the proposed photoswitchable surface topography is demonstrated in Scheme 2. A hydrogel stripe with an impregnated topography and a non-responsive but ultrathin cover layer will swell upon a light trigger in a way that leads to a lateral stretching of the surface and in turn to an alteration of the surface topography up to a complete diminishment of the nanosized surface features. By that, a switching between extreme wetting cases is envisioned. The light trigger in combination with limited gel dimensions in the z-direction will ensure a fast response in order to ensure that the gel response is not delayed and thus not constituting the time limiting factor in the wetting change.

The gel stripe will be composed of a thermosensitive polymer that bears photoswitchable arylazopyrazol (AAP) moieties. These groups change their polarity upon a light trigger leading to a change in the lower critical solution temperature of the polymer network they are attached to. If the temperature is kept close to this transition temperature, the LCST change is enough to induce the volume phase transition of the gel and thus to induce a strong response. Anisotropic swelling, i.e. preferred swelling of the gel in the lateral dimension, will be ensured by the presence of additional liquid crystal forming functions or by utilizing high aspect ratio filling material (e.g. inorganic fibers) with the aid of magnetic fields or shear forces, respectively, during the gel casting. The AAP moiety will be introduced to the polymer structure by post polymerization modification using thiolactone equipped polymer precursors or via

copolymerization of respective monomers. The formation of the desired gel specimens will be done by first generating a nanostructured surface onto which the gel is casted. After removing the original nanostructured master, an ultrathin, polymeric top layer is grafted onto the stripe under maintenance of the surface topography. As a starting point for the generation of the surface topography masters, a plasma-backed, controlled wrinkling of a PDMS surface will be applied. Here, a PDMS specimen is stretched followed by plasma treatment that generates a thin SiO_2 top layer on the material. Due to the difference in E-module between the bulk and this SiO_2 top layer, a subsequent stress release will lead to a wrinkling of the surface.

The proposed project includes further the design and implementation of a device with which dynamic wetting phenomena can be investigated. Focus lies here on the coupling of contact angle detection with the light trigger in an environment that ensures reversible gel swelling. With this device, evolution of contact angles of simple liquids upon switching of gel topography will be investigated in exemplary cases.
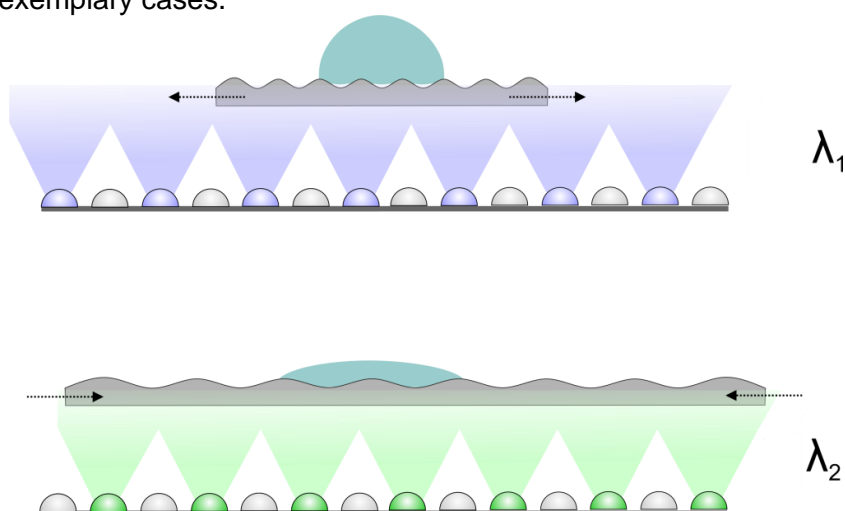
Scheme 2. Proposed general scheme for a fast and repeated photoswitching of a structured surface topography. The latter is part of a hydrogel that reversibly swells in the lateral dimension upon a phototrigger. The nano-structured surface of the gel is covered with a varying, non-responsive ultrathin top layer.

| WP	Content	Year 1				Year 2				Year 3			
		1	2	3	4	1	2	3	4	1	2	3	4
1	Photoresponsive surface topographies	▓	▓	▓	▓	▓	▓	▓	▓				
1.1	Hydrogels design and characterization	░	░	░	░								
1.2	Hydrogels with switchable surface topography					░	░	░					
2	Contact angle measurement setup						▓	▓	▓				
3	Dynamic wetting							▓	▓	▓	▓	▓	▓
4	Droplet movement									▓	▓	▓	▓
5	Publications and final report								▓				▓
M1	Photoresponsive gel with anisotropic swelling				██								
M2	Photoswitchable surface topography / setup for dynamic wetting							██					
M3	First dynamic wetting measurements									██			
M4	Proof-of-principle phototriggered droplet movement											██	

WP1: Photoresponsive surface topographies

WP 1.1 - Hydrogel design and characterization

At the start of the proposed project stands the synthesis of the hydrogel stripes. A multitude of structural parameters has to be controlled in order to finally obtain a material that responds to light with high amplitude and without delay. The basic structure of the gel is depicted in Scheme 3 on the right. The thermoresponsive polymer backbone will be formed by respective *N*-isopropylacrylamide (or alternative (meth-)acrylate) units while permanent crosslinks will be provided in situ by a special protocol developed by Espeel et al. which involves the reaction of polymer bound thiolactone units with multifunctional amines.[60] Finally, arylazopyrazol (AAP) for the photoswitching and liquid crystal forming motifs (LC) or anisotropic stiff fillers for an anisotropic swelling behavior will be included. While the basis for the LC structure will be poly(benzyl-L-glutamate), which is able to form a nematic phase with long-range order upon exposure to a magnetic field[61], the stiff anisotropic fillers can be nanocellulose or peptide fibers.[62] These fillers will be oriented within the gel matrix by appliying shear forces (Scheme 4). AAP can be attached to the precursor polymer by the previously mentioned thiolactone groups with respective functional acrylates in a post-polymerization step or by copolymerizing respective functional monomers (Scheme 3). The compounds needed for the gel anisotropy will be simply blended into the gel bulk. Leaving a few unreacted thiolactone units will also provide the opportunity to address these groups later on to attach the non-responsive top layer on the wrinkled surface (see WP 1.2).

Response studies will be first performed on non-crosslinked polymers in solution using dynamic light scattering with temperature control. Further response studies will be performed on the gels under variation of the gel composition and dimension in order to test the amplitude, kinetics and direction of the gel response. Here, crosslinking density, density of photosensitive AAP groups, content of LC groups or anisotropic fibers as well as gel stripe dimensions are in focus. It is especially important to identify the maximum gel thickness that is still allowed to ensure a fast response without much delay. The swelling and shrinking of the gels can be monitored with a video camera. The fabrication of the stripes will be done by simple mixing and casting of the single components onto pre-shaped templates. If shear needs to be applied, fast injection into a preformed gel mold can be done (Scheme 4). In collaboration with Bart-Jan Ravoo of the University of Münster we will also systematically select the most effective AAP derivatives and will design respective monomers or acrylate derivatives needed for the post-polymerization modification (Scheme 3).

The opportunity for a double modification of the thiolactone equipped polymer precursors allows us further not only to introduce AAP functions but also to tune the polymer solubility and thus swelling behavior of the resulting gel.[16] In the same way, the AAP functions are introduced, that is, by Michael type addition of a respective acrylate to the thiol groups that are released upon reaction of the crosslinking diamine with the thiolactone units, other functions can be introduced that can steer the transition temperature of the gel. Hydrophilic acrylates like those carrying oligo(ethylene glycol) substituents will raise this temperature, while more hydrophobic species, such as *n*-octyl acrylate will cause a respective decrease.
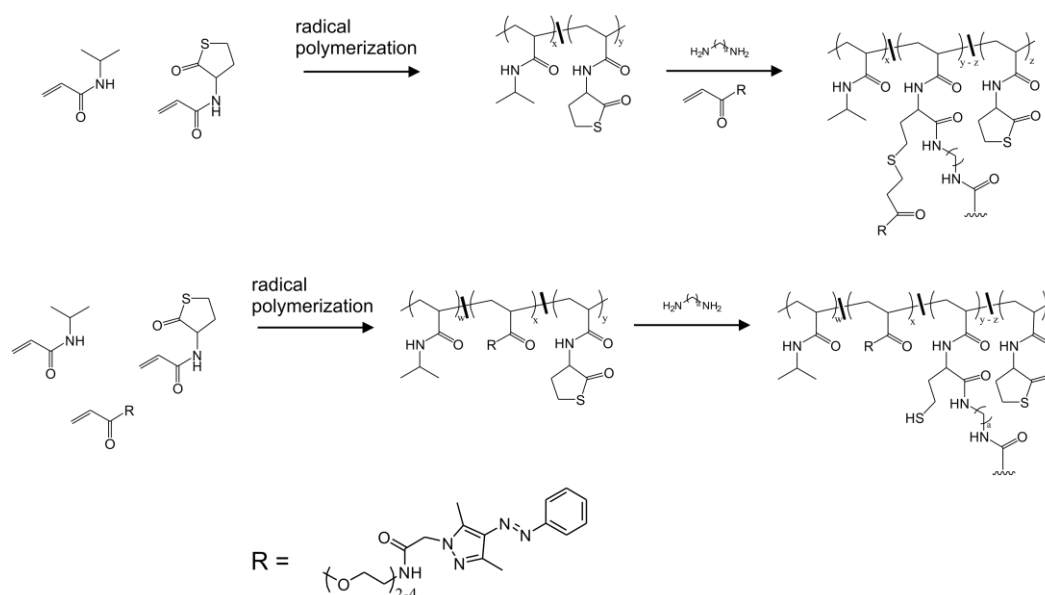
Scheme 3. Synthetic routes towards the desired hydrogel structures. The remaining thiolactone units will be used later on to attach polymerization initiators to the gel surface for the grafting of the non-responsive top layer (see Scheme 4).

WP 1.2 - Hydrogels with switchable surface topography

With the optimum gel recipe from WP 1.1, specimens can now be produced that have an impregnated surface topography. The basis for the generation of specific surface patterns is the controlled wrinkling of PDMS surfaces. Here, PDMS precursor stripes will be stretched to a certain extent followed by plasma treatment that generates a thin SiO_2-layer on the surface of the stripe. Subsequent release of the sample from the stretched state will cause a wrinkling of the surface (Figure 5) due to the now present bilayer structure. Specimens generated via this method will serve as masters for the replication of the patterns into the hydrogel structure. The simplest pattern obtainable are uniaxially oriented sinusoidal wrinkles whose amplitude and wavelength can be easily controlled by the extent and the general way of stretching of the PDMS precursor, the thickness of the latter and the conditions of the plasma treatment.[49] However, radial as well as chevron like patterns can also be generated via this method as well as perpendicularly overlapping patterns.[49] By the proposed method we are thus able to generate a broad library of surface topographies that can be used later on for the wetting studies. Generated surface patterns will be characterized mainly by atomic force microscopy. Custom made stretch apparatuses (Figure 6) will be used to ensure homogenous surfaces with a minimum of surface pattern defects. The absence of the latter can be controlled by optical microscopy.
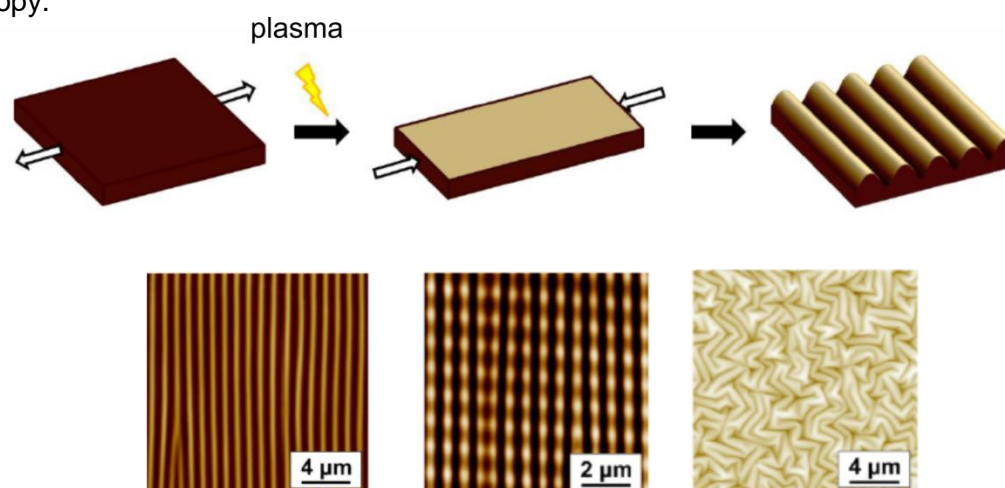

Figure 5. Principle concept for the controlled wrinkling of PDMS substrates. The bottom images shows a selection of patterns that are accessible via this method.[52]
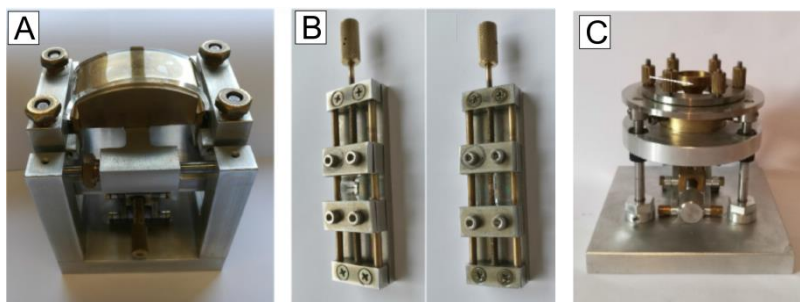
Figure 6. Stretch apparatuses for the fabrication of the wrinkle master specimens: A) bending apparatus; B) elongation apparatus; C) 360 ° stretching apparatus.

After generation of the masters, the gel component mixtures will be casted onto the wrinkled master surface (Scheme 4). As mentioned earlier, gel casting can be performed in the presence of a magnetic field, aiding the orientation of the liquid crystal domains, or under shear to orient the anisotropic fillers. Sufficient shear forces are mostly occurring already during injection of a respective viscous liquid through a small channel.[63] By these measures, the anisotropic swelling of the gel is ensured. When the permanent crosslinking via the reaction of the thiolactone units with the diamine is finished, the master is removed and the gel surface will be characterized by liquid mode AFM in order to verify the successful transformation of the wrinkle pattern. In a final step a non-responsive top layer will be introduced to the wrinkled surface of the gel. That top layer must remain as thin as possible in order to rule out any influence of the different E-moduli of the surface layer and the bulk of the gel stripe. This will ensure an uniaxial stretching of the wrinkled top layer without the occurrence of curling. Respective trials will be part of this work package. Very thin layers can be obtained by grafting techniques which introduce polymer brushes of varying chain lengths to the surface. As it is important to ensure a high brush density in order to avoid gel surface exposure, and thus an alteration of the surface chemistry, upon stretching of the gel stripe, we will stick to the grafting-from technique. We will make use of unreacted thiolactone groups at the gel surface that can be addressed by amino functionalized polymerization initiators. The polymer type will be varied including non-polar materials like polystyrene and more polar (but not water soluble) types like acrylamides. A crucial aspect for the introduction of initiating sites and the following grafting step is the choice of reaction medium. The two steps should not make a swelling medium exchange necessary as this could lead to damage of the gel stripe due to osmotic pressures occurring during the exchange. Thus, the grafting procedure must take place either in water or a medium in which the gel is not swellable and that does not mix with water. If this is ensured, the gel can be safely brought in contact with the reaction medium without any structural damage. In order to further ensure that only the top face of the gel stripe is equipped with polymer brushes, the gel stripe will be kept in a confined space during the process revealing only the top face to the reaction medium. A successful grafting including assessment of the brush layer thickness can be verified by contact angle measurements and scanning electron microscopy (SEM). Maintenance of the surface topography will be verified again by AFM.

Finally, the surface topography evolution upon the photoswitch needs to be assessed. The question here is, to which extent the uniaxially oriented wrinkles disappear, or in the case of other patterns or wrinkle orientation, how the patterns change. Here, also kinetics will be monitored. For that purpose, we will collaborate with Kirsten Harth of the University of Magdeburg who wants to build up a high speed imaging facility based on photometric mapping techniques within the framework of the SPP. Parallel to that, surface topographies of intermediate swelling states can be investigated by shock-freezing of the gel specimen at the different states of swelling with subsequent subjection to cryo-SEM.
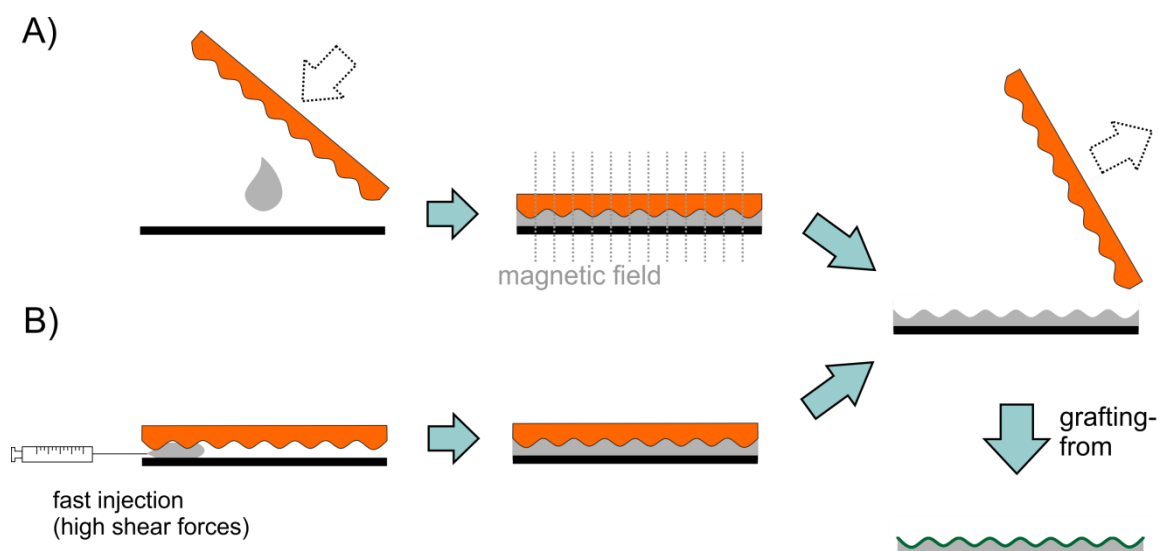
Scheme 4. Process for gel casting with wrinkle pattern replication: A) Process for the gel stripes containing LC species. The gelation mixture is first casted on a support followed by printing with the master specimen. Curing occurs in the presence of a homogenous magnetic field. B) Process for the gel stripes containing high aspect ratio filling material. The gelation mixture is injected into a gap between a flat support and the master specimen. The high shear forces during injection will cause an alignment of the fillers. For both approaches, a thin, non-responsive top layer is grafted from the resulting gel specimen.

WP 2: Contact angle measurement setup

Basis of the dynamic wetting studies will be a simple contact angle measuring device including a CCD camera and respective software for contact angle detection and analysis. The setup for the gel can be directly placed on the measurement table of the device and be operated independently from it. The design of the setup is depicted in Scheme 5. An array of light emitting diodes of proper wavelengths is deposited at the bottom. On top of that a small UV-permeable and thermostatable housing that contains the swelling liquid is placed. This housing, together with additional UV-permeable glass slides, confines the gel in the z-dimension, preventing it from floating freely around. The glass slides are lifting the gel stripe so that it partially sticks out of the swelling medium making its edge being accessible for the recording camera. The whole arrangement is designed in a way that all parts are kept as thin as possible so that the light signal does not need to penetrate through a thick layer of liquid before reaching the gel bulk.
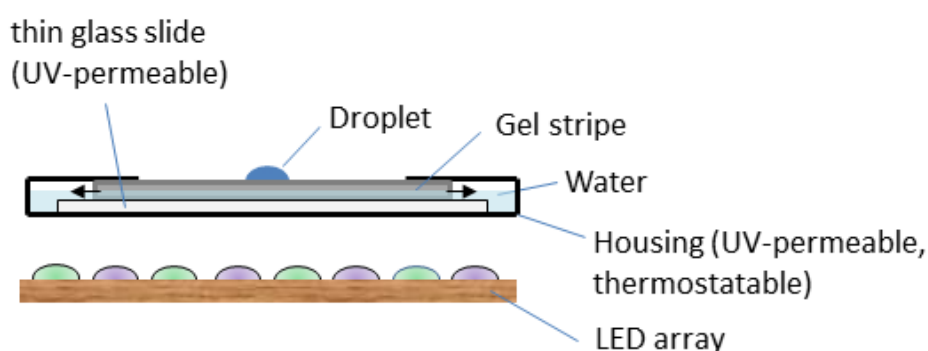
Scheme 5. Cross section through the proposed measurement setup for dynamic wetting studies.

In collaboration with Prof. Doris Vollmer from the Max-Planck-Institute for Polymer Research in Mainz we will also test wether wetting phenomena on our photoswitchable surfaces can also be monitored via confocal microscopy.

WP 3: Dynamic wetting

Given the fact that dynamic wetting on switchable surfaces has been scarcely investigated so far, we want to demonstrate use cases in WP3 for the monitoring of wetting kinetics of a liquid droplet being placed on a surface that can be switched between two extreme wetting cases. The main benefit of our concept is the quick response of the nanostructured surface upon an external stimulus. Thus, fast and repeated switching allows us to bring a deposited droplet repeatedly into a non-equilibrium state thereby permanently triggering a respective wetting adaptation. Repeated deposition of fresh droplets or exchange of surface bearing specimens is thus not necessary. The generation of master specimens with defined surface topography happens independently from the hydrogel stripe preparation. Thus, any kind nanostructured surface can in principle be implemented in our concept in order to study diverse wetting situations. Within the scope of the project, we will mainly use surface topographies that can be generated by the controlled wrinkling of PDMS substrates as described above. Yet, the surface topographies accessible by this method are already quite diverse and allow for the selection of concrete analytic targets. The planned switch between a rough and a smooth surface (disappearance of the wrinkle patterns upon stretching of the gel specimen) is envisioned to provide a transition between two surfaces with very different wetting conditions (e.g. Cassie and Wenzel states). Particular experiments in the framework of dynamic wetting, limiting ourselves to water as wetting liquid, will be:

- *Wetting kinetics for in situ generated/altered surface roughness without surface chemistry change* – the influence of wrinkle wavelength and amplitude on the kinetics will be investigated
- *Periodic switching of surface roughness with defined frequency* – How well is the droplet response coupled to the surface topography change?
- *Kinetics on anisotropic wetting cases, that occur on surfaces with uniaxially oriented wrinkles* – how do wetting kinetics differ in different lateral directions
- *Contact angle hysteresis* – a very quick switch of the surface topography relative to the response time of the deposited droplet will allow us to measure the boundaries of the contact angle range (advancing/ receding contact angle).

Additionally, static wetting experiments can be followed:

- *Influence of surface roughness and roughness pattern on wettability changes for changing surface chemistry* – Here, pairs of gel specimens with identical topography but differing surface chemistry will be applied.

Experiments will also be performed on hydrogel substrates without patterned surface in order to determine the influence of the change of top layer brush density that occurs upon the stretching of the gel stripe, as this could also have an influence on the contact angle.

For the dynamic wetting experiments it is crucial that the topography change is not the time limiting factor. Consequently, the droplet response time may have to be adjusted. This can be done by using water soluble polymers that will change viscosity within the droplet. Here, we want to concentrate on polymers of same chemical composition but differing architecture and molecular weight. By that, viscosity can be changed within a certain range without changing the concentration of the dissolved material. Concentration effects on the contact angle the droplet is adopting can thus be ruled out. Suitable types of polymers are polyethyleneimine and poly(ethylene glycol). Both types are water soluble and at the same time available in linear as well as branched form.

WP4: Droplet movement

With the proposed concept of an optically switchable surface topography we want to demonstrate a new way for inducing liquid droplet movement on selected surfaces. For that we will use the same setup as described in WP2 with the difference that a moving mask will be introduced between the LED array and the hydrogel stripe. By that we can apply a highly localized irradiation that will make the gel stripe swell only at one particular position at the time (Scheme 6). That narrow irradiation zone, being significantly smaller than the droplet dimensions, is used to induce different topographies and in turn contact angles at the two sides of the droplet which induces a lateral force on the latter. The movement of the narrow irradiation zone along the long axis of the stripe will eventually make the droplet move along the surface without applying any external mechanical force. In contrast to our previous work on droplet movement[41], where a static gradient was embossed into the surface, the gradient will be induced on demand and can be controlled temporally.

Droplet velocities and the general efficiency of the droplet motion depend on a number of parameters. The droplet volume, the contact angle differences between the two topography states and opposing viscous forces[37,64–66] are among those, which can be controlled by us. A throrough study will be performed including systematic variation of all of these parameters. Again, viscosity modifiers based on water soluble polymers with different molecular weight and architecture will be applied.
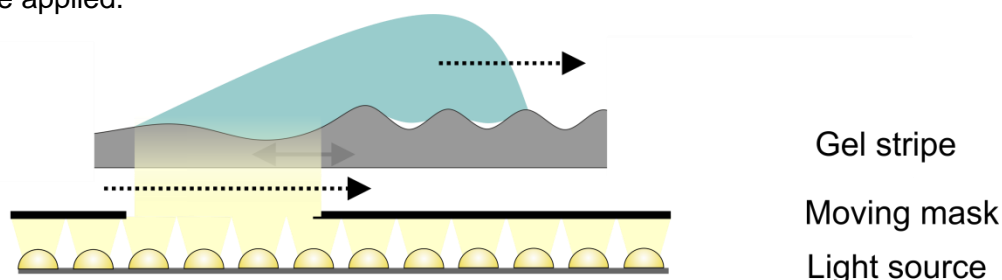
Scheme 6. Concept for a phototriggered movement of a droplet on the surface of photoresponsive hydrogel. Spatially resolved light exposure of the gel stripe leads to topography change only at specific areas of the stripe. A moving mask lets the light ray move along the entire stripe. By that, droplet movement is induced.

2.4   Data handling

Project relevant data will be kept for 10 years.

2.5   Other information

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2.6   Descriptions of proposed investigations involving experiments on humans, human materials or animals as well as dual use research of concern

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2.7   Information on scientific and financial involvement of international cooperation partners

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2.8   Information on scientific cooperation within SPP 2171

Prof. Bart-Jan Ravoo from the University of Münster will bring in his expertise on photoswitchable arylazopyrazole compounds and will aid us in synthesizing the respective material. Prof. Svetlana Santer from the University of Potsdam, is planning, like us, to create a system on photoswitchable surface topographies in order to study the respective dynamic

wetting behavior. In contrast to our approach, she will illuminate azobenzene containing polymer films with optical interference patterns to generate the respective topography. It is planned in close collaboration with Prof. Santer to compare our results concerning wetting behaviour obtained with our photoswitchable surfaces. On top of that, Prof. Santer will include arrays of photosensitive posts in her investigations. These posts can also be used by us to create alternative surface topographies for our gel stripes which cannot be created by the controlled wrinkling of PDMS. Together with Prof. Doris Vollmer from the Max-Planck-Institute for Polymer Research in Mainz, we will test, wether our photoswitchable surfaces are suitable for confocal microscopy as complementary tool for studying wetting phenomena. We will also make use of high speed imaging techniques that will be built up by Kirsten Harth of the University of Magdeburg. Additional collaboration is envisioned to be created after the project start. Here, we plan to find partners within the SPP that can aid us in the theoretical description of our experimental findings.

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4   Requested modules/funds

4.1   Basic Module

4.1.1   Funding for Staff

1 PhD student - TVL-13; 67 %; 36 Monate   *129.645 €*

For the multitude of tasks that have to be accomplished within the proposed work packages, a PhD student is needed for the whole duration of the project. The student should have expertise and a respective master's degree in the field of macromolecular or physical chemistry with a special focus on responsive materials and/or interfaces.

Student assistant; 18 Personenmonate   *35.600 €*

In order to fulfil the proposed project goals student workforce is needed to tackle all routine tasks. This includes repetition of syntheses for a continuous provision of the desired polymers, precursors and wrinkle pattern masters as well as execution of repetitive routine measurements such as polymer cloud points or contact angle recordings.

4.1.2   Direct Project Costs

4.1.2.1   Equipment up to Euro 10,000, Software and Consumables

Chemicals, glassware, parts for contact angle measurement setup
and miscallenous consumables   *30.000 €*

The proposed sum is composed of the costs for the purchase of required chemicals including monomers, liquid crystalline functional compounds, nanocellulose fibers and the viscosity modifying polymers as well as solvents, chromatography material and additional chemicals for synthesis workup. Parts for the assembly of the contact angle measurement device (LEDs, UV permeable glass slides, custom made housing, peltier elements, …), AFM tips and standard consumables (pipettes, tissue for cleaning, disposable gloves, etc.) are needed.

4.1.2.2   Travel Expenses

Conference fees and travel costs   *7.000 €*

The visit of international conferences is required to present project results in front of an international professional audience and to be able to follow newest developments in the respective field of research. In the first year, work on the hydrogel design and characterization with a proof of principle of the uniaxial swellability and, accompanied to that, the light triggered diminishment/change of the surface topography will be presented. At the end of the second year the described use cases on dynamic wetting and finally at the end of the project duration the light-triggered droplet motion will be presented. Conferences of choice will be such that focus on or include (stimuli-responsive) polymer materials like the annual International Symposium on Stimuli-Responsive Materials or the IUPAC World Polymer Congress, and interfaces like the annual ECIS conference and the ACS Colloid and Surface Science Symposium.

Travel costs will also include the trips to the SPP workshops and meetings, as well as to the labs of our collaboration partners.

4.1.2.3   Visiting Researchers (excluding Mercator Fellows)

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4.1.2.4   Expenses for Laboratory Animals

-

4.1.2.5   Other Costs

-

4.1.2.6   Project-related publication expenses

Publication costs   *2.500 €*

Publication costs include fees for open access journals.

4.1.3   Instrumentation

4.1.3.1   Equipment exceeding Euro 10,000

-

4.1.3.2   Major Instrumentation exceeding Euro 50,000

-

4.2   Module Temporary Position for Principle Investigator

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4.3   Module Replacement Funding

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4.4   Module Temporary Clinician Substitute

-

4.5   Module Mercator Fellows

-

4.6   Module Workshop Funding

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4.7   Module Public Relations Funding

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5   Project requirements

5.1   Employment status information

| Stefan Reinicke | PhD | Contract until 31.03.21 |
| Alexander Böker | Professor | Unlimited contract |

5.2   First-time proposal data

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5.3   Composition of the project group

Stefan Reinicke	Dr. rer. nat. (Macromolecular Chemistry)	Project leader, Fraunhofer IAP	Contract until 31.03.21
Alexander Böker	Prof. (Physical Chemistry)	Professor, University of Potsdam	Unlimited contract

5.4   Cooperation with other researchers

5.4.1   Researchers with whom you have agreed to cooperate on this project

Prof. Bart-Jan Ravoo of the University of Münster, Germany, will provide us arylazopyrazole derivatives and will give further advice with respect to the investigations on the photoswitching part. Prof. Svetlana Santer of the University of Potsdam also plans to investigate wetting behavior on photoresponsive surfaces. In a close collaboration we will compare our results with the data that is generated by her approach. Furthermore, Prof. Santer will provide additional surface topographies that cannot be generated by us. Prof. Doris Vollmer from the Max-Planck-Institute for Polymer Research in Mainz will test, wether our photoswitchable surfaces are suitable for studying wetting dynamics with the help of confocal microscopy. Kirsten Harth of the University of Magdeburg is planning to build up a high speed imaging facility in her lab that we also plan to make us of.

5.4.2   Researchers with whom you have collaborated scientifically within the past three years

In the last three years, we had a cooperation with the institute of bioorganic chemistry at the University of Düsseldorf (Prof. Jörg Pietruszka), Prof. Ulrich Schwaneberg (RWTH Aachen) and Prof. Bart-Jan Ravoo (University of Münster) as well as a loose cooperation with Prof. Andreas Taubert, PD Dr. Burkhard Schulz as well as Prof. Svetlana Santer (all University of Potsdam), and Prof. em. Gerald Brezesinski (MPI for Colloid and Interface Research). Internationally, cooperation occured with Prof. Filip Du Prez and Prof. Bruno de Geest (University of Ghent, Belgium).

5.5   Scientific equipment

Our lab equipment includes a fully equipped synthesis lab for low molecular weight organic compounds and polymers obtainable by radical polymerization including respective analytics. A UV/VIS spectrometer is available, a thermostatable dynamic light scattering device, a state-of-the art AFM as well as a modifiable contact angle detection device. For the generation of the wrinkle masters, custom-made stretch apparatuses as well as a plasma oven exists. (Cryo-)SEM and dynamic light scattering are available at the Fraunhofer-Institute for Applied Polymer Research. Supplementary analytical tools will be accessible via our collaboration partners.

5.6   Project-relevant cooperation with commercial enterprises

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5.7   Project-relevant participation in commercial enterprises

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6   Additional information

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