

Project Description – Project Proposals

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Dynamic covalent polymers as switchable substrates for changing the wetting/dewetting behavior on demand

Project Description

1 State of the art and preliminary work

State of the art

Switchable and adaptive materials gained much interest over the last years.^[1] Different materials have been designed, synthesized and their properties were studied in detail.^[2] First applications of these switchable materials were already investigated ranging from self-healing^[3] to shape-memory polymers.^[4] Nevertheless, one major aspect is also the utilization of switchable materials (as well as surfaces) to influence / control the wetting/dewetting behavior with different fluids.^[5-6] Firstly, the switchability of the wetting by a stimulus, which can, e.g., be temperature or changes of the pH-value, were studied.^[7-8] Furthermore, the reversibility of such processes as well as their underlying chemical and physical properties were investigated in detail.^[9-11] The knowledge gained was utilized to fabricate materials suitable for the water-oil separation.^[6]

Generally, stimuli-responsive polymers seem to be ideal for the design of switchable surfaces and, consequently, tuning the corresponding wetting behavior with different liquids.^[1, 12] As a prerequisite, the polymers have to be able to change their chemical structure accompanied with changes of their physical properties by the application of an external stimulus (e.g., heat, light). Consequently, highly adaptive surfaces can be designed capable of changing their wetting behavior depending on the external environment.^[5] However, only a limited number of polymers were already applied within this context. Thus, azobenzenes^[13-15] as well as spiropyrans^[16-17] were incorporated into polymeric structures in order to enable a switching *via* irradiation with (UV-)light. This irradiation results in an isomerization and, consequently, in a change of the wetting behavior. Furthermore, ferrocene containing polymers can be applied for switching the wettability by oxidation.^[18] Additionally, polyelectrolytes (*i.e.* ionic polymers) were applied as stimuli-responsive polymers.^[19] This type of polymers can either be triggered using temperature (if the polymers feature a lower critical solution temperature – LCST-behavior) and by changing the pH-value, respectively.^[20-22] Such a behavior can chemically be attributed to the acid or amino groups, which can either be protonated (amine in acidic conditions) or deprotonated (acid in basic conditions). The change of the molecular structure results in a change of the polarity and, consequently, in a change of the interaction with fluids. Within this context, mainly water was utilized; however, it is also possible to change the interaction with oil based systems like hexadecane.^[23] One recent example is depicted in **Figure 1** showing the switching of a polyelectrolyte block-copolymer, which changes the interaction with either water or oil in dependency of the pH-value.^[24] This phenomenon can be monitored easily by measuring the contact angle between the water (or oil) droplet with the surface of the polymer. Additionally, the wetting behavior can also be monitored using time-dependent measurements showing that the wetting with water is much faster at lower pH-value. In contrast, at neutral pH, nearly no wetting could be

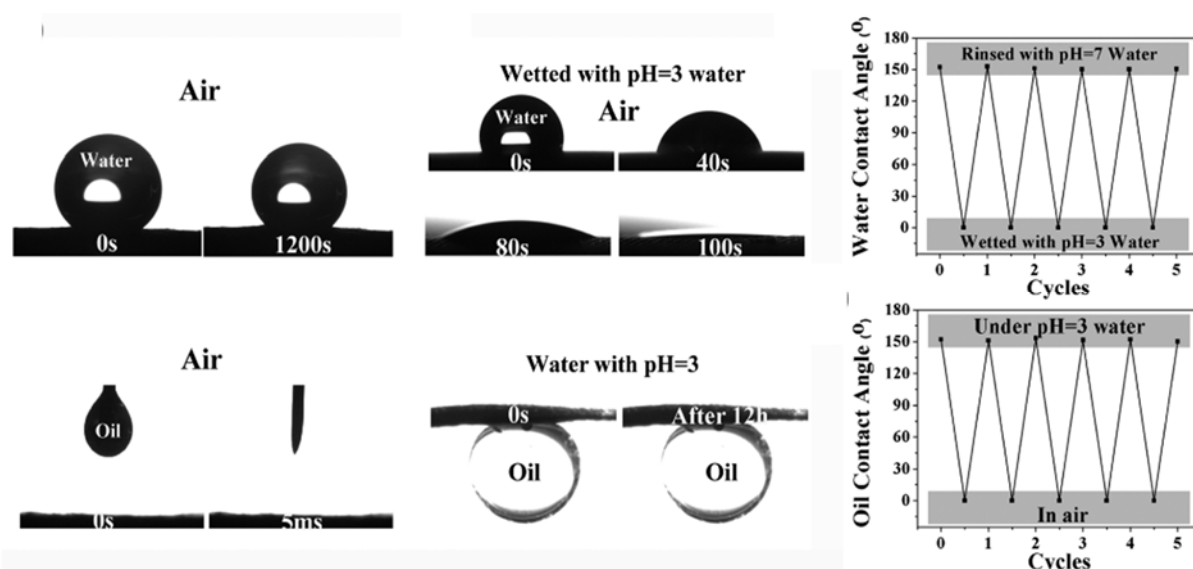


Figure 1: Schematic representation of the interaction of a block copolymer featuring an ionic block with water (above) and oil (bottom). Furthermore, it was revealed that the contact angle at the three-phase contact line can change during cycles (middle above). Additionally, the behavior can be influenced by the pH-value (right), which is furthermore reversible (Figure reprinted from Ref. [24]).

observed. Finally, this stimuli-responsive polyelectrolyte can also be reversibly switched. If the stimulus is removed (change of low pH-value to a higher one) the original properties can be regained and *vice versa*, the behavior can be triggered again by applying stimulus multiple times.^[24]

Noteworthy, the number of different polymers applied as material for selectively switching of the wetting / dewetting behavior is still very limited, particularly if covalently crosslinked materials are considered.^[6]

Thus, this project aims at implementing new reversible covalent polymers as responsive material to influence the wetting behavior and to reveal general structure-property relationships *via* different microscopic and spectroscopic approaches. Here, predominantly the changes of the physical properties and the chemical structure will be studied (also independently from each other) during switching of these polymers by Raman spectroscopy and coherent anti-Stokes Raman scattering (CARS) microscopy.

For this purpose, it is planned to utilize stimuli-responsive materials for the (reversible) changing of the wetting behavior. As stimuli-responsive material, dynamic covalent polymers will be utilized,^[25] which were already shown to feature reversible properties switchable by an external stimulus.^[26] Those stimuli range from heat, light, pH-changes to redox reactions.^[26] Typical structural elements in this context are Diels-Alder reaction and other cycloadditions.^[27-28] Furthermore, disulfides, esters as well as imine based systems can be utilized for this purpose.^[29] Typical applications of such systems are self-healing^[30] or shape-memory polymers.^[4] However, these materials were not applied as substrate for wetting / dewetting processes so far, even they feature a high potential due to the drastic changes in polarity.

Preliminary work

The fruitful collaboration between the two principle investigators resulted in several publications in the last years (thereof 14 in the last three years). The joined research focusses mainly on the analysis of reversible covalent (as well as supramolecular) polymers, which were studied considering their self-healing ability. Within this context, the **AG Hager** focused on the synthesis of the polymeric materials, whereas the molecular, chemical and physical mechanisms were analyzed by the **AG Popp**. Exemplarily, dynamic covalent polymers based on the thermally reversible Diels-Alder reactions were synthesized by the controlled radical polymerization technique ATRP.^[31] The reversibility of the Diels-Alder reaction (equilibrium between open and

closed state) could be influenced by choosing different kinds of polarity of the comonomers as well as by varying the Diels-Alder units.^[32-33] The underlying molecular mechanism could be revealed using Raman spectroscopy in combination with two dimensional correlation analysis of the temperature-dependent measurements.^[34-35] This method could be firstly applied for self-healing polymers revealing fundamental chemical and molecular mechanisms (opening and closing of the Diels-Alder unit) as well as the correlation to the physical properties (flow of the material resulting in a closure of the damage and, thus, self-healing behavior).

Furthermore, it was also possible to study other dynamic covalent bonds. One intensively studied material is based on thermally reversible thiol-ene reactions. Firstly, it was possible to demonstrate the healing of those materials.^[36] Using Raman spectroscopy the opening of the bond can be visualized revealing a correlation to the change of the physical properties of the material shown by rheology measurements.^[36-37] Furthermore, the temperature-dependent shift of the equilibrium between the opened and closed state could be analyzed using Raman spectroscopy. Finally, very fundamental molecular, chemical as well as physical properties of the healing could be revealed using coherent anti-Stokes Raman scattering (CARS) microscopy.^[38] Thus, the method was applied as an imaging technique compared to classical light scattering. For the CARS-analysis, the double-bond signal of the thiol-ene acceptor was utilized and it could be demonstrated that the occurring chemistry and the overall flow of the material do not necessarily correlate (**Figure 2**).

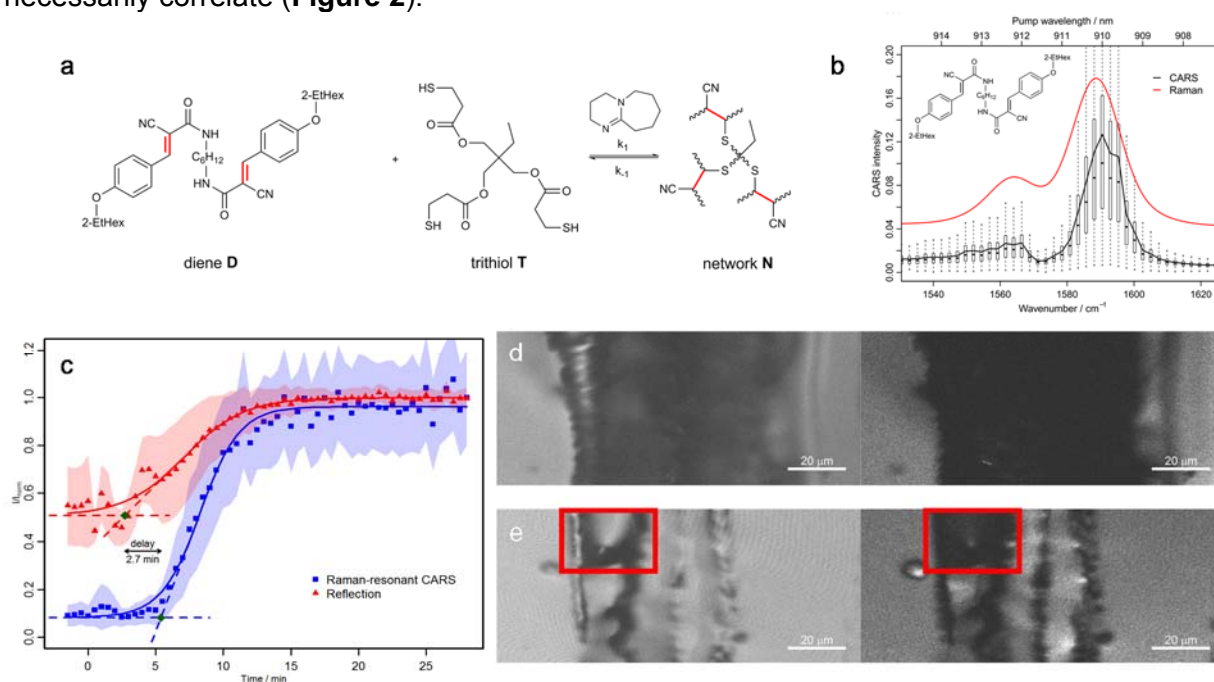


Figure 2: Schematic representation of the investigation of a thiol-ene based self-healing polymer (a) by CARS-spectroscopy (CARS and Raman spectrum depicted in b). The self-healing process (starting from the damaged material depicted in d) was monitored by optical (left pictures in d and e) and CARS microscopy (right pictures in d and e) showing that after six minutes (e) the overall healing process is faster compared to the process depicted in the CARS images. The delay time of the onset in the healing process was determined to be 2.7 minutes (c) (Reprinted from Ref. [38]).

Finally, the applicants were also able to design dynamic covalent polymers, which can be triggered either by a change of the pH-value or temperature. These moieties include imines,^[39] acylhydrazones^[40] as well as oximes,^[41] which will be all utilized within the proposed project. By comparing these systems, it could be revealed that the increasing stability of the covalent bond (imines over acylhydrazones to oximes) results also in different self-healing behavior.

1.1 Project-related publications

The publication track record of the applicants demonstrates their capability to successfully implement the proposed work. This is particularly reflected in the selected following recent publications:

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

- R. Geitner, F. Bekele Legesse, N. Kuhl, T. W. Bocklitz, S. Zechel, J. Vitz, **M. D. Hager**, U. S. Schubert, B. Dietzek, M. Schmitt, **J. Popp**, “Do you get what you see? Understanding molecular self-healing”, *Chem. Eur. J.* **2018**, 24, 2493-2502.
- J. Ahner, D. Pretzel, M. Enke, R. Geitner, S. Zechel, **J. Popp**, U. S. Schubert, **M. D. Hager**, “Conjugated oligomers as fluorescence marker for the determination of the self-healing efficiency in mussel-inspired polymers”, *Chem. Mater.* **2018**, 30, 2791-2799.
- N. Kuhl, M. Abend, R. Geitner, J. Vitz, S. Zechel, M. Schmitt, **J. Popp**, U. S. Schubert, **M. D. Hager**, “Urethanes as reversible covalent moieties in self-healing polymers”, *Eur. Polym. J.* **2018**, 104, 45-50.
- R. Geitner, S. Götz, R. Stach, M. Siegmann, P. Krebs, S. Zechel, K. Schreyer, A. Winter, **M. D. Hager**, U. S. Schubert, S. Gräfe, B. Dietzek, B. Mizaikoff, M. Schmitt, **J. Popp**, “Hydrogel-embedded model photocatalytic system investigated by Raman and IR spectroscopy assisted by density functional theory calculations and two-dimensional correlation analysis”, *J. Phys. Chem. A* **2018**, 122, 2677-2687.
- J. Ahner, M. Micheel, R. Geitner, M. Schmitt, **J. Popp**, B. Dietzek, **M. D. Hager**, “Self-healing functional polymers optical property recovery of conjugated polymer films by uncatalyzed imine metathesis”, *Macromolecules* **2017**, 50, 3789-3795.
- S. Zechel, R. Geitner, M. Abend, M. Siegmann, M. Enke, N. Kuhl, M. Klein, J. Vitz, S. Gräfe, B. Dietzek, M. Schmitt, **J. Popp**, U. S. Schubert, **M. D. Hager**, “Intrinsic self-healing polymers with high E-modulus based on dynamic reversible urea bonds”, *NPG Asia Mater.* **2017**, 9, e420.
- R. Tepper, S. Bode, R. Geitner, M. Geitner, M. Jäger, H. Görls, J. Vitz, B. Dietzek, M. Schmitt, **J. Popp**, **M. D. Hager**, U. S. Schubert, “Polymeric halogen-bond-based donor systems showing self-healing behavior in thin films”, *Angew. Chem. Int. Ed.* **2017**, 56, 4047-4051.
- N. Kuhl, M. Abend, S. Bode, U. S. Schubert, **M. D. Hager**, “Oxime crosslinked polymer networks: Is every reversible covalent bond suitable to create self-healing polymers?”, *J. Appl. Polym. Sci.* **2016**, 133, 44168.
- R. Geitner, J. Kötteritzsch, M. Siegmann, T. W. Bocklitz, **M. D. Hager**, U. S. Schubert, S. Gräfe, B. Dietzek, M. Schmitt, **J. Popp**, “Two-dimensional Raman correlation spectroscopy reveals molecular structural changes during temperature-induced self-healing in polymers based on the Diels-Alder reaction”, *Phys. Chem. Chem. Phys.* **2015**, 17, 22587-22595.
- N. Kuhl, S. Bode, R. K. Bose, J. Vitz, A. Seifert, S. Hoepfner, S. J. Garcia, S. Spange, S. van der Zwaag, **M. D. Hager**, U. S. Schubert, “Acyldiazones as reversible covalent crosslinkers for self-healing polymers”, *Adv. Funct. Mater.* **2015**, 25, 3295-3301.

1.1.2 Other publications

n/a

1.1.3 Patents

n/a

1.1.3.1 Pending

n/a

1.1.3.2 Issued

n/a

2 Objectives and work programme

2.1 Anticipated total duration of the project

The proposed project is a newly proposed project with an anticipated duration of 36 months. We aim for starting together with the SPP 2171 on October 1st, 2019.

2.2 Objectives

The proposed project has two main objectives (**Figure 3**):

- 1) Implementation of dynamic covalent polymers as switchable substrates;
- 2) Implementation of novel analysis method predominantly coherent anti-Stokes Raman scattering (CARS) microscopy, which will enable a temporal as well as spatial investigation of the changes of the chemical structure within the polymer as well as the wetting of the liquids.

Therefore, several reversible covalent moieties, which can be switched by either pH-value or temperature, should be incorporated into a polymeric structure. These units should range from rather stable ones (*i.e.* oximes), which are hardly addressable by an external stimulus, to very labile moieties (*i.e.* imines). In contrast to pH-switchable polymers, changes of the pH value will first not result in charged species (*e.g.*, carboxylate or ammonium). In addition, a second step will be possible if the formed amine (in case of the imine) or the other nitrogen species are protonated. Moreover, these polymers can also be triggered by heat leading to exchange reactions, which could potentially allow the polymer to “react” to the wetting liquid. The obtained dynamic covalent polymers will be studied regarding their interaction with different liquids, *i.e.* water and oil (hexadecane). Hereby, the interaction between these two phases as well as their influence on each other will be studied in detail. For this purpose, a range of different methods will be

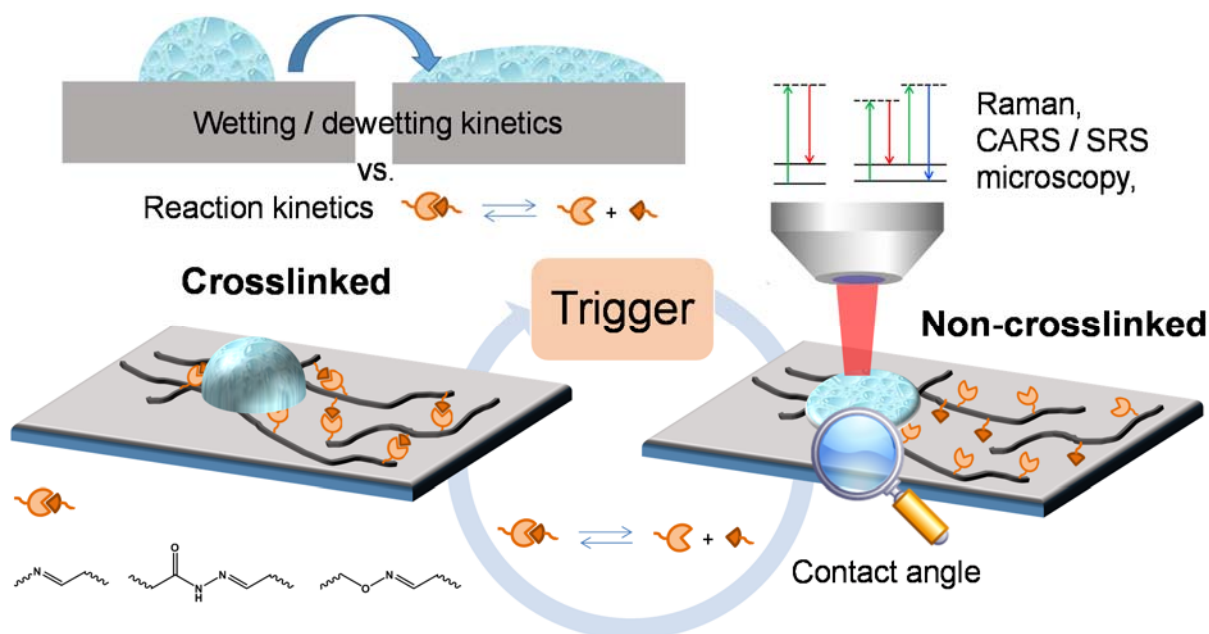


Figure 3: Schematic representation of the proposed project: Dynamic covalent moieties (imines, acylhydrazones, oximes) will be incorporated into a polymeric structure (left) resulting in a polymer film featuring a certain interaction with liquids (water or oil). During application of an external stimulus (mainly temperature or pH-value) the dynamic covalent moiety can be addressed resulting in an opening of the bond (or exchange reaction – not depicted here) and a change of the interaction with the liquid (right). This behavior will be studied using different techniques, in particular CARS microscopy enabling temporal and spatial resolution of the different phenomena. Consequently, this approach allows studying the kinetics of the wetting / dewetting process independently from the reaction kinetics (left top).

applied, such as standard techniques like contact angle measurements. Furthermore, CARS microscopy will be utilized for the first time in this context allowing the simultaneous monitoring of changes of the chemical structure and the wetting process independently from each other. Both processes (*i.e.* switching of the chemistry – also locally) and the wetting can be decoupled from each other providing kinetics of the reaction (in case of reactive wetting) as well as kinetics of the wetting.

In order to study these general structure-property-relationships and to understand physical and chemical phenomena in this context, it is required to focus on the following five different aspects within the project:

- 1) *Reversible covalent moiety*: Three major units will be utilized for this project, namely, imines, acylhydrazones as well as oximes will be applied, which all were already shown to be reversible under certain circumstances. However, the addressability is different for all those groups. Whereas imines can be easily addressed, *e.g.*, by slightly acidic water,^[42] oximes requires much harsher conditions like trifluoroacetic acid.^[43] Furthermore, those functional groups can also be triggered using thermal activation. However, a different mechanism of activation was observed depending on the utilized trigger. Whereas pH-triggering results in an opening of the bond and the reformation of the educts, the thermal activation will lead to exchange reactions between different moieties and, thus, no pronounced structural changes. Nevertheless, the polymer properties will change during thermal activation. Thus, one major aspect investigated in the project will be the different addressability and its influence on the wetting behavior.
- 2) *Type of polymer as well as the polymer design*: Crosslinked polymer networks featuring the reversible unit as crosslinker as well as linear polymer with the reversible moiety in the side-chain will be studied. Furthermore, homo- and copolymers will be investigated as well. Comonomers can be utilized to adjust the interaction with liquids ranging from hydrophobic to hydrophilic. This change will also influence the addressability of the reversible unit, since a phase separation can also decrease (or increase) the interaction of the liquid with the reversible moieties. Finally, it is also planned to synthesize block copolymers featuring the possibility to induce a defined phase-separation. Additionally, nano-structuring of the materials by laser ablation is possible, which would be performed in cooperation within the SPP (Prof. F. Müller, FSU Jena).
- 3) *Wetting with different liquids (water as well as oil)*: Generally, contact angle measurements will be performed showing the general interaction of the three phases (polymer, liquid, air) at their interface. This analysis method will also be performed time dependent, since water (in particular if the pH-value is changed) can also lead to a change of the polymeric structure and, thus, of the contact angle (*i.e.* reactive wetting).
- 4) *Implementation of CARS microscopy*: CARS microscopy will be applied as a novel powerful tool to study the (chemical) response of the polymer to the liquid. Additionally, it allows valuable insights into the spatial and temporal wetting behavior, which can provide new aspects in the field of wetting – dewetting. The combination of CARS microscopy with contact angle measurements will allow accessing detailed information on the relationship of the structure with respect to the physical properties.
- 5) *Switchability by external stimulus*: Finally, the major aspect of the proposed project is the investigation of the switchability of the polymeric substrate by external stimuli. First of all, it will be investigated, if the applied liquid (water or oil) is a potential stimulus for the reversible polymer. For instance, water can address the imine bond resulting in a bond cleavage and a change of the polymer properties (*i.e.* the polymer is getting more polar promoting a wetting with water). However, this behavior will strongly depend on the polymer itself, since superhydrophobic materials are more hardly addressable as compared to hydrophilic ones. Furthermore, the pH-value will be utilized as external trigger for the dynamic covalent moieties. Hereby, the addressability is completely different for all utilized reversible structural elements and a systematic study will be performed showing at which pH-value which type of bond can be addressed in which kind of polymeric structure revealing general structure-property (interaction with the

liquid) relationships. The same principle will also be studied for thermal treatment as activator for the chemical bond. In order to study the influence of the stimulus in detail, it is planned to follow the contact angle during stimulus application. Furthermore, time dependent CARS microscopy will be performed revealing spatially resolved structural insights. Consequently, the wetting speed depending on the chosen stimulus can be monitored and can also be correlated to the reaction speed of the chemical responsiveness.

2.3 Work programme incl. proposed research methods

The above-described objectives require an extensive knowledge and experience in the field of macromolecular synthesis as well as physico-chemical characterization of polymeric materials. These requirements are highly fulfilled by the two principal investigators of this project. Whereas the group of Dr. Martin D. Hager is highly active in the field of polymer synthesis and in particular in the design of dynamic covalent polymers, the group of Prof. Dr. Jürgen Popp has ample expertise in the characterization of polymeric materials using spectroscopic methods such as Raman (micro)spectroscopy or CARS microscopy. The project will be divided into four work packages, which are summarized in **Figure 4**.

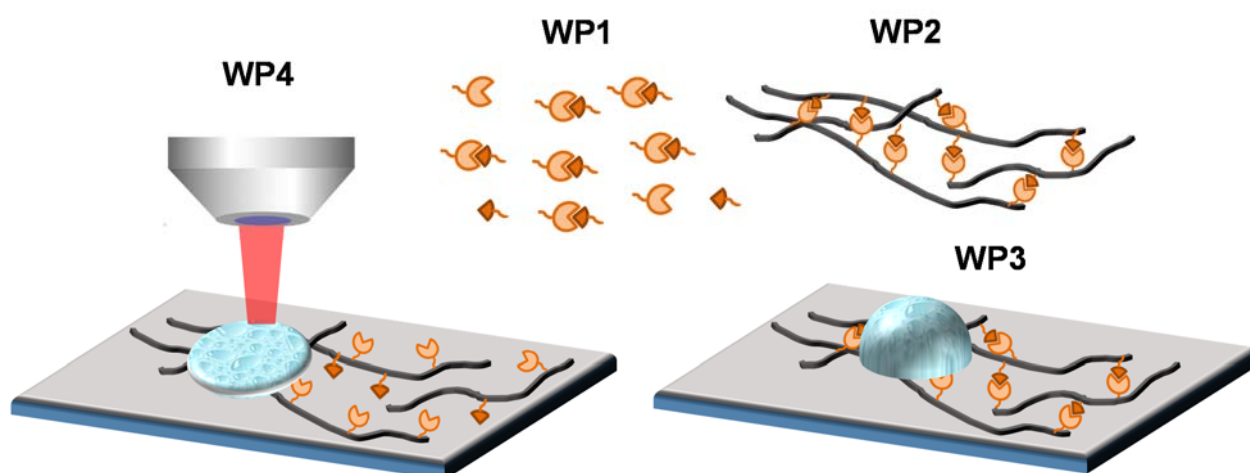


Figure 4: Schematic representation of the workflow of the proposed project: Within **WP1** monomers and model system will be synthesized, which will be incorporated into polymer architectures within **WP2**. The characterization of the interaction with liquids and the wetting behavior will be studied in **WP3** and finally, the switchability of the polymer film and the corresponding change in the wetting behavior will analyzed in **WP4**.

WP 1: Synthesis of monomers and model systems

The first WP includes the synthesis of monomers, which will be utilized later (**WP2**) for the preparation of polymers. Furthermore, model systems featuring a similar chemical structure without any polymerizable groups will also be synthesized within **WP1**, in order to study the reversibility in a more controlled manner. As reversible elements a toolbox containing three different moieties will be utilized. These are summarized in **Figure 5** and will be imines, acylhydrazones as well as oximes. The moieties are chosen due to their known reversible character, which can be obtained using either temperature or pH-value as the corresponding triggers.^[44-45] Furthermore, their switchability or stability on the other hand, differs between these three moieties. Thus, the stability against water/pH or temperature increases from imines over acylhydrazones to the most stable one, oximes. Imines can be triggered by slightly acid water resulting in an opening of the bond and a reformation of the educts (amine and aldehyde). In contrast, the bond cleavage in oxime requires harsh conditions, e.g., strong acids like trifluoroacetic acid.^[43, 46]

In addition, the reversibility will be further tuned by the choice of substituents at the reversible unit. Thus, the difference between aliphatic and aromatic substituents will be evaluated within the proposed project. It can be expected that aromatic substituents result in a higher degree of shielding of the bond and, thus, a reduced addressability. This effect will be further enhanced in

case of imines, since a conjugated π -system will be more stable compared to aliphatic imines. Consequently, this approach will enable us to synthesize a toolbox of different dynamic moieties, which feature different degrees of stability against water and temperature. Furthermore, it is planned to utilize carbonyl compounds featuring a deuterium atom at the carbonyl carbon enabling us to visualize this vibration in more detail using CARS microscopy (see **WP3** for details). For this purpose, a literature known procedure will be applied.^[47]

All types of reversible units will be incorporated into monomeric structures enabling a later synthesis of functional polymers. As monomer motifs mostly (meth-)acrylates will be applied, since these unit can be introduced easily by esterification. Furthermore, these monomer structures feature the benefit to be polymerizable in a controlled fashion by different controlled radical polymerization techniques. Furthermore, a variety of different possible comonomers enable a fine-tuning of the final properties of the polymer films and consequently of their properties, in particular hydrophilicity or hydrophobicity.

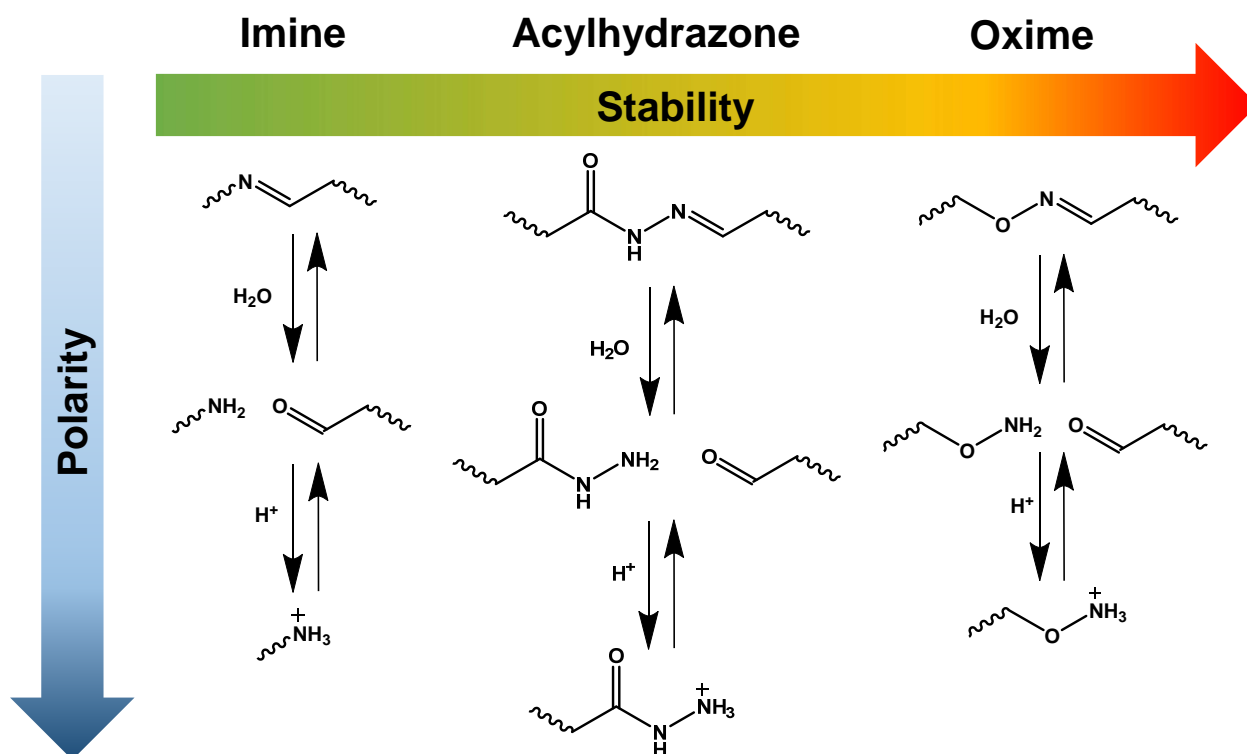


Figure 5: Schematic representation of the three different reversible moieties applied in the proposed project. From left (imines) to right (oximes), the stability against water/pH-change as well as against temperature increases allowing a systematic investigation of the different addressabilities of the moieties on the wetting / dewetting behavior of the polymers. Furthermore, the polarity of the moieties increases dramatically during bond opening. Additionally, a potential second step induced by protonation of the nitrogen bond is depicted, which can be reached at very low pH-values enabling a two-step mechanism of changing the wetting behavior during stimulus application.

WP 2: Synthesis of the (co)polymers

The second working package, which is closely related to **WP1**, will focus on the preparation of polymers and copolymers. The combination of **WP1** and **WP2** will provide the material toolbox for the later characterization of the physical and chemical behavior of the polymers as well as their interaction with liquids (additionally during application of a stimulus).

Within **WP2**, a variety of different polymer architectures will be synthesized (**Figure 6**). First of all, the reversible moiety will be incorporated as side chain into polymers. Furthermore, it is intended to prepare polymer networks as well, in which the reversible moiety acts as crosslinker between polymer chains. The difference in these two types of polymers will also result in different material properties, different interactions with liquids and furthermore, a different accessibility and addressability of the reversible moieties.

Within the side-chain functionalized polymers, different classes will be synthesized. Firstly, homopolymers of the monomers of **WP1** will be prepared. These polymers feature a high density of functional groups making them ideal candidates for an efficient switching during application of the stimulus (see **WP4** for details). However, the material properties are hardly be adjustable (only by the choice of substituents on the functional group), since only the reversible moiety influences the later properties. For this purpose, it is planned to prepare copolymers as well. In this case, a second monomer will be copolymerized with the functional one resulting in statistical copolymers. Within this approach, it is possible to adjust the material properties like hydrophilicity by the choice of the appropriate comonomer. A toolbox of different commercial monomers (**Figure 7**) enables us to prepare materials over the entire spectrum of polarity, which will also influence the addressability of the reversible moieties. Within this context, it is planned to prepare a small library of different compositions in order to evaluate structure-property-relationships.

Furthermore, it is also planned to prepare copolymers featuring an excess of one moiety required for the crosslinker formation. Exemplarily, additional amine functions will be incorporated into an imine containing copolymer in order to enhance the temperature induced exchange reaction. Furthermore, the polarity of the polymer will change due to the incorporation of such polar groups. Finally, a stimulus application could potentially result in a movement of the amino groups to the polymer-water interface, since these groups are highly polar. This chemical phase separation will change the interaction between substrate and liquid and will also enhance the influence of the droplet onto the polymer structure (liquid as stimulus for reactive wetting). However, the exact behavior cannot be predicted and will be studied using contact angle measurements in combination with CARS microscopy (see **WP3**).

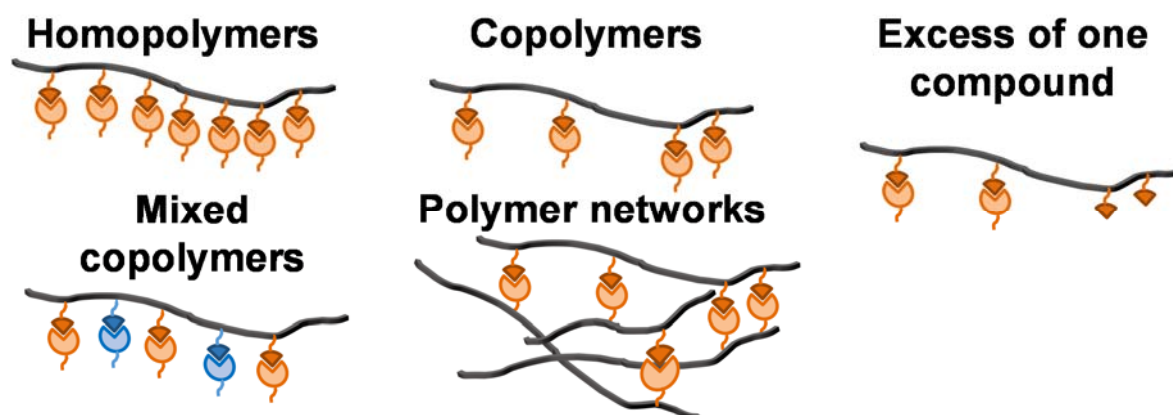


Figure 6: Schematic representation of targeted polymer structures within the proposed project. The basic systems are homo- and copolymers as well as polymer networks. As advanced polymer architectures mixed copolymer featuring at least two different reversible moieties (e.g., imines and oximes) will be synthesized within the project. Finally, it is also planned to introduce an excess of one compound.

If required additional covalent crosslinker are introduced in or to prevent the dissolution of the polymer film. Furthermore, the last approach will focus on the preparation of mixed copolymers. Hereby, two different reversible moieties will be incorporated into one polymer structure. This approach enables us to switch the interaction with a liquid (or the material properties in general) stepwise. Exemplarily, a copolymer containing imine and oxime units will be addressed in two steps, if the pH-value is decreased. Firstly, the imines will be activated and at much lower pH-value, the oximes can also be addressed. Nevertheless, it is also possible that both types of reversible units influence each other resulting in a different addressability to the pure homopolymers. In particular, the reformation of the dynamic covalent moieties during the back-reaction can result in a kind of molecular ordering as described in solution experiments for other systems and imines.^[48-49] Therefore, the stimuli-responsive behavior of such systems will be studied in

cyclic experiments. However, this effect was not studied up to now and will be evaluated in the project after the basic systems are characterized and understood in detail.

All in all, a variety of different polymers will be synthesized within **WP2**. In order to access these structures, it is planned to utilize controlled radical polymerization techniques enabling an efficient and controlled preparation of the polymer materials. Furthermore, it allows the synthesis of polymers with a specific molar mass and a low dispersity. Additionally, defined end groups can be introduced enabling a sufficient synthesis of block copolymers as already shown in previous work.^[50-52] In particular, the reversible addition chain-fragmentation polymerization (RAFT) and the atom-transfer radical polymerization will be applied, since both techniques are well established in the group of Dr. Martin D. Hager.^[31-32, 52]

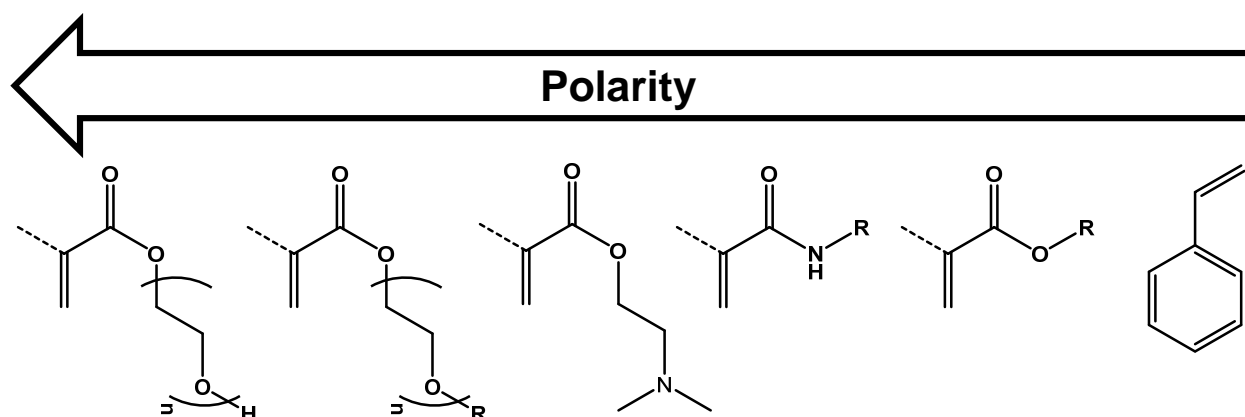


Figure 7: Schematic representation of the comonomers, which will be utilized for the synthesis of copolymers as well as copolymer networks. From left to right: ω -Hydroxy-poly(ethylene glycol) (meth-) acrylate, ω -alkoxy-poly(ethylene glycol) (meth-)acrylate (R = alkyl); 2-(dimethylamino)ethyl (meth-)acrylate (which is also pH-switchable); (meth-)acrylamides (R = alkyl); (meth-)acrylates (R = alkyl) and styrene.

WP 3: Characterization of the wetting behavior

The third WP will focus on the characterization of the polymeric substrates and in particular their wetting behavior. Within this context, the interaction of the material with different liquids (mainly water and oil) will be studied in detail. The effect of surfactants would also be very interesting, but the required investigations are far beyond the scope of the proposal and, thus, we would like to perform those experiments in cooperation within the SPP.

The main characterization method of the proposed project will be contact angle measurements. By measuring the contact angle at the three-phase contact line, information about the hydrophilicity / hydrophobicity can be achieved. The three phases are the polymer substrate, the liquid and air. As liquids, water and oil, i.e. hexadecane, will be utilized. The contact angle measurements will be performed static as well as dynamic. Furthermore, the static contact angle measurements will be performed time-dependent, since it can be expected that for certain polymeric systems the interaction of the liquid (in particular water) with the reversible groups within the polymer can gradually change the hydrophilicity / hydrophobicity of the polymer and, consequently, the contact angle. This time-dependent change will be utilized to investigate the kinetics of the interaction of the polymer substrate and the liquid, which will also provide information of the surface tension as a function of time.^[53] Furthermore, the contact angle measurement results will be utilized to obtain information about the wettability applying Young's equation.^[54] Furthermore, the contact angle measurements will be utilized to calculate typical physical properties of the polymers. Thus, the surface free energy will be obtained using either the Neumann model,^[55-56] the Fowkes^[57] or the extended Fowkes, the Owens-Wendt-model.^[58] Additionally, the Zisman method will be applied revealing the critical surface tension.^[59] The obtained information will be utilized to construct general structure-property relationships. Furthermore, the obtained physical parameters will be provided for diverse projects in the priority programme, which can extend their research on understanding of ongoing physical processes.

In cooperation with the group of Prof. Frank Müller (FSU Jena), who would also like to participate in the SPP 2171, it is planned to analyze the effect of nanostructured surfaces on the

wettability of the new polymeric materials. For this purpose, his group will nanostructure our polymers in a controlled manner by laser ablation. Afterwards, this effect will be analyzed by contact angle measurements (static and dynamic) as well as hysteresis measurements. However, these results will be compared with non-structured surfaces, which will be analyzed in a similar manner.

Besides contact angle measurements, CARS microscopy will be applied as a new tool to characterize the wetting behavior on a molecular level in order to correlate it with the chemical structure of the polymeric surface (particularly important for the tasks described in **WP4**). CARS is a nonlinear Raman variant which allows for real time imaging of intensity changes of characteristic Raman peaks over large areas up to cm^2 at diffraction limited spatial resolution. Thus, the application of this method enables monitoring chemical reactions *via* highlighting single specific molecular vibrations (with large Raman scattering cross sections, *i.e.* polar molecular groups) involved in the chemical reaction. These vibrations will be identified prior to the CARS analysis *via* linear Raman spectroscopy, which suffers from long acquisition times. Here, we will combine standard contact angle microscopy and CARS microscopy in one setup to simultaneously characterize the hydrophilicity / hydrophobicity with molecular structural information and/or structural changes upon wetting and dewetting. The combination of these two microscopic approaches provides valuable insights about the interaction of the liquid and the solid phase and for addressing the question of a potential reactive wetting. The phenomena of reactive wetting can be exemplified *via* the reaction of a water droplet with imine bonds. This reaction changes both the molecular structure as well as the substrate-droplet interaction. Changes in the molecular structure can be monitored by CARS microscopy *via* imaging the C=N vibration, which features a high Raman intensity,^[60-61] and since this process can only be observed at the droplet polymer interface contact angle measurements allows a detailed investigation of the changes of the droplet-polymer interaction as well as the hydrophilicity / hydrophobicity of the polymer (**Figure 8**). Furthermore, the combination of CARS and contact angle measurements enables a 3D analysis of such reactive wetting processes.

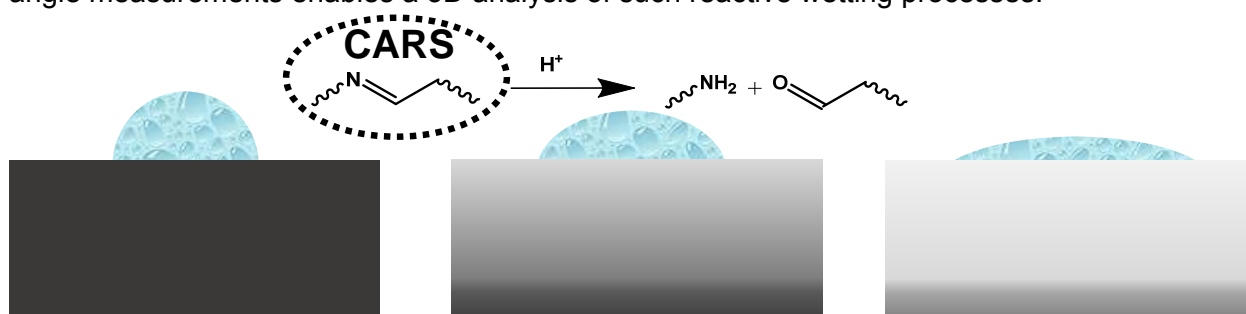


Figure 8: Schematic representation of the utilization of combined CARS and contact angle measurements for this project. As example, monitoring intensity changes of the C=N vibration (imine bond; marked with dotted circle) *via* CARS is depicted. During application of a stimulus (*e.g.*, change of the pH-value; decrease of the value shown from left to right), the imine bond is converted to an amine as well as to an aldehyde. The structural changes, *i.e.* decrease of the amount of imine, can be monitored using CARS microscopy revealing a lower signal intensity. The change of the resulting properties (hydrophilicity / hydrophobicity) as well as the changes in the interaction of the polymer and the droplet can be revealed using contact angle measurements. The correlation of both using one common microscopic setup can result in general structure-property-relationships.

We will specially utilize *epi*-detected CARS (E-CARS)^[62] to suppress a possible non-resonant CARS background due the droplet. The molecular CARS contrast can be further enhanced by applying deuterated solvents as droplets or by usage of partially deuterium marked substituents on the reversible units. CARS microscopy is particularly suited to monitor CH-stretch vibrations due to their large Raman scattering cross sections. In this context labeling with deuterium and detecting the corresponding CD stretch vibrations, which also exhibit a large Raman cross section and most importantly appears in an otherwise wavenumber silent region, is a powerful approach to distinguish between molecules of interest from the polymer surrounding. Exemplarily, a potential reactive wetting can simply be monitored using these CD vibrations, if deuterium oxide is utilized as droplet. Furthermore, the pH-stimulus can be also achieved by applying deuterated acids resulting in the possibility to monitor the structural changes *via* temporally resolved CARS microscopy. One further option would be the synthesis of aldehydes containing a

deuterium at the carbonyl carbon resulting in functional groups (imine, acylhydrazone or oxime) with directly bound deuterium. The synthetic protocols were recently described in literature and will be applied in the project.^[47] The molecular CARS contrast enhancement can further be extended by introducing other molecular groups with large Raman scattering cross sections and Raman transitions in the wavenumber silent region like, e.g., $\text{-C}\equiv\text{N-}$ triple bonds,^[38] which can be installed at an aromatic aldehyde utilized for the formation of either imine, acylhydrazone or oxime. Thus, the application of such Raman tags (*i.e.* stable isotope labeling or addition of single molecular bonds with a large Raman scattering cross section), leading to vibrations within the wavenumber silent region allows for the targeted monitoring of molecules of interest.^a

All information obtained by contact angle and CARS measurements (additionally standard Raman microscopy will be performed as well) will be correlated with each other resulting in the possibility to draw general structure-property relationships (**Figure 9**). Additionally, the analysis methods will also be utilized within **WP4** in order to understand the general influence of switching of the molecular structure on the resulting properties and their correlation with the wetting behavior. These relationships can further be supported by potential other or more detailed analysis methods within the SPP. Consequently, the PIs are highly motivated to provide materials for potential cooperation partners in order to obtain more insights into the behavior of this new kind of materials. Additionally, the CARS technique can also be utilized for other projects within the SPP providing insights into the behavior of other materials, in particular switchable ones, and to correlate those results with the results obtained in our project.

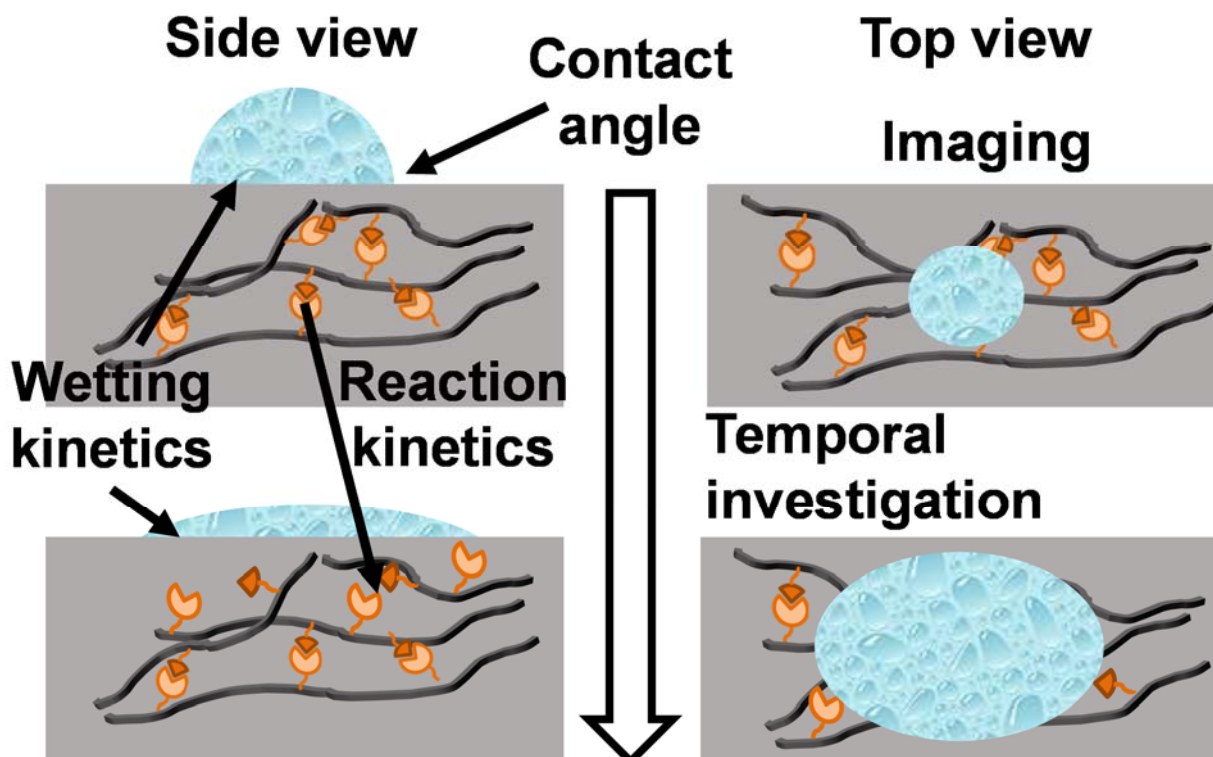


Figure 9: Schematic representation of different parameters investigated within the proposed project. Using contact angle measurements, the wetting behavior as well as physical properties will be determined. Furthermore, CARS microscopy will be utilized in order to perform molecular properties imaging of the substrate and to correlate these results with the contact angle measurements revealing information about the wetting kinetics and the reactions of the reversible moieties within the polymer structure. For this purpose, time-dependent measurements will also be performed.

^a In case it turns out that no Raman resonances with sufficiently high scattering cross section can be identified to generate CARS images with high molecular contrast (*i.e.* with negligible non-resonant CARS background), it is planned to use the non-linear Raman method SRS (stimulated Raman scattering), which is experimentally more complex compared to CARS.^[63] SRS provides the same information as CARS but does not lead to a non-resonant background. However, SRS microscopy is experientially more challenging and, thus, we will mainly focus on CARS microscopy.

WP 4: Stimuli-responsive behavior of the polymeric substrates

The last working package will be the central element of the proposal. It is strongly connected to the characterization part **WP3**, since the analytical techniques described in **WP3** will be applied in order to understand the ongoing processes and the resulting changes. Generally, **WP4** will focus on five different aspects regarding the stimuli-responsiveness of the materials and the resulting changes of the materials properties, e.g., interaction with the liquid. Firstly, the possibility of reactive wetting will be elucidated in detail. Furthermore, the influence of an external stimulus will be analyzed. Within this context, the third point of interest will be studied, which is the correlation between the two different processes ongoing (change in wetting behavior vs. kinetics of the stimuli-responsive behavior). The fourth parameter will be the reversibility of the stimuli-responsiveness. Thus, it will be studied, if the original properties can be regenerated after the stimulus is removed. The last point of interest is a step-wise addressability of the polymers, which will be performed using the mixed copolymers featuring two different reversible groups from **WP2**.

As mentioned, the first part of **WP4** will focus on the possibility of reactive wetting. In principle, the chosen reversible moieties can be addressed by water resulting in an opening of the chemical bond and, consequently, in a change of the materials properties, e.g., the interaction with a liquid. However, the reaction only takes place under acid conditions and, thus, the degree of reactive wetting is expected to be low. On the other hand, it can be increased by using a more polar polymer design as well as very labile imines bonds. The degree of reaction wetting will be investigated using Raman spectroscopy and CARS microscopy in combination with contact angle measurements. These methods allow a detailed analysis of the behavior of the polymer during contact with a liquid, *i.e.* water. These experiments will also be performed time-dependent, which would allow determining the reaction kinetics of the reactive wetting process. For the CARS measurements, the C=N bonds of the reversible moieties (imine, acylhydrazones as well as oxime) will be utilized for monitoring the process. As alternative, deuterium oxide is applied as liquid to selectively visualize the interaction of water with the polymer.

The influence of a stimulus on the polymeric material as well as on the interaction of the solid state and liquid will be studied in the second part of **WP4** (**Figure 10**). Mainly, the change of the pH-value as well as temperature increase will be applied as potential stimuli. Generally, these stimuli should result in a change of the molecular structure of the polymer due to the addressability of the dynamic covalent bonds within the polymeric structure. The change of the molecular structure will result in other material properties as well as a changed interaction with liquids. It is expected that polymers become more polar during the application of a stimulus resulting in a more hydrophilic behavior. From previous work and literature reports,^[39-40, 43-44] we expect that both stimuli could potentially result in a different change of the materials properties. The decrease of the pH-value will, at a certain value, result in an opening of the reversible bond and, thus, in a change of the interaction with a liquid due to the formation of aldehydes and amines / acylhydrazides / hydroxylamines. Notably, all moieties can also be protonated in a second step allowing a two-step process of changing the interaction of the substrate and the liquid. In contrast, increasing the temperature will predominantly lead to exchange reactions between two functional groups as described as a typical property of vitrimers.^[64] Consequently, the structure does not change over time. Nevertheless, the properties will change during stimuli application. Furthermore, one functional moiety can be utilized in excess. By this manner, the polymer can “react” to the liquid – for instance amines present in excess can move to the surface increasing the interaction with water (comparable to self-replenishing surfaces).^[65] However, the influence on the interaction of the substrate and liquid cannot be predicted so far. Currently, three possible options are possible: First of all, no change of the interaction is possible. Secondly, the exchange reactions can enhance the possibility for reactive wetting, if water is utilized as droplet. Finally, the exchange reaction can also result in a sufficient property change and, consequently, in a change of the interaction with the liquid. All three options will be considered and will be analyzed during the proposed project. For this purpose, temperature-

and time-dependent contact angle and CARS microscopy measurements will be performed. Thus, the behavior of the structure as well as the interaction between solid and liquid phase at the three-phase line will be elucidated in detail.

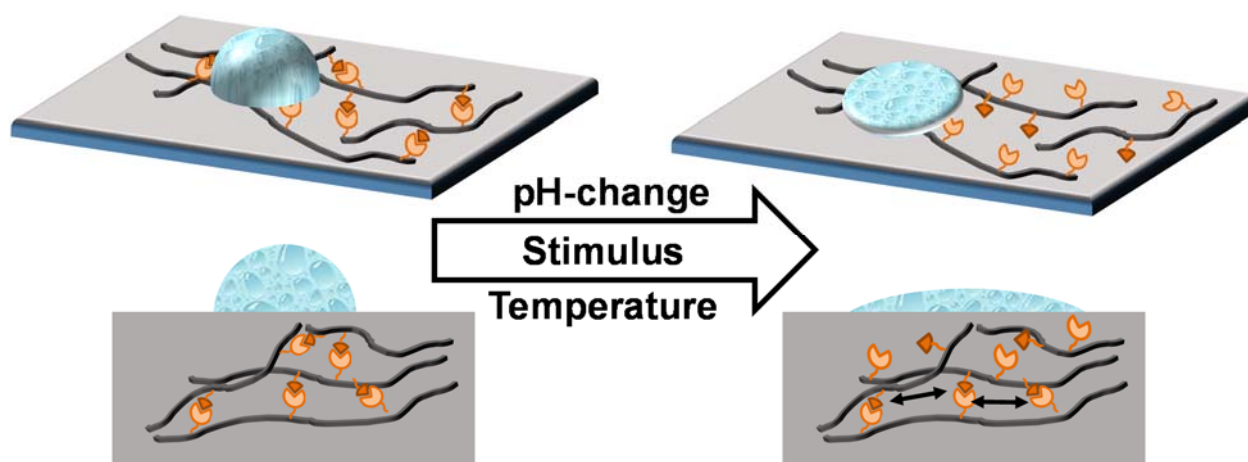


Figure 10: Schematic representation of the potential changes during stimuli application. As stimuli, change in the pH-value as well as increase in temperature will be applied, which will directly influence the interaction of the polymeric substrate and the liquid at the three-phase line. The stimulus can either induce an opening of the bonds as well as exchange reactions between different moieties shown by means of the arrows.

The third part of **WP4** will focus on the ongoing chemical and physical processes (see **Figure 11**). Mostly, two processes will be analyzed within this study. Thus, the behavior of the functional groups during stimulus application (reaction) and the response of the material in respect of the wetting behavior will be studied. In particular, the time-dependent changes and, consequently, the basic kinetics are of interest. For this purpose, contact angle measurements as well as CARS microscopy will be applied. CARS microscopy can provide insights into the wetting speed as well as in case of reactive wetting into the progress (and kinetics) of the process. For this purpose, the C=N vibrations will be utilized. Furthermore, the partially deuterated samples featuring a deuterium at the functional group will be also applied for this project part. Generally, the two processes (reaction and change in wetting) will feature a dependency from each other. Firstly, the onset of the reaction after stimuli application will be studied as well as the progress of the reaction. Afterwards, the correlation with the changes of the interaction with the liquid will be performed. Therefore, the information of the CARS measurement will be correlated with the results from the contact angle analysis *via* implementing CARS microscopy and contact angle analysis in one common setup (**WP3**).

The fourth important parameter will be the reversibility of the stimuli-responsive behavior. Within this study, two major aspects will be addressed: First of all, the question arises, if the polymer structure can be reformed after the stimulus is removed. Thus, an increase of the pH-value or the decrease of the temperature to the original value can also result in the original properties. Otherwise, the properties cannot be recovered after removing the stimulus due to irreversible side-reactions or non-exciting reversibility of the dynamic reaction within the polymers. This process will firstly be studied by static contact angle measurements in order to see the behavior in detail. Furthermore, the chemical behavior of the polymer will be studied using CARS microscopy (using the same vibrations as mentioned above; C=N and C-D). If a reversible behavior will be observed, the kinetics of the reversibility will be studied in detail providing information about reaction speed as well as wetting speed and their dependency from each other. Furthermore, multiple cycles of stimulus on-and-off will be performed.

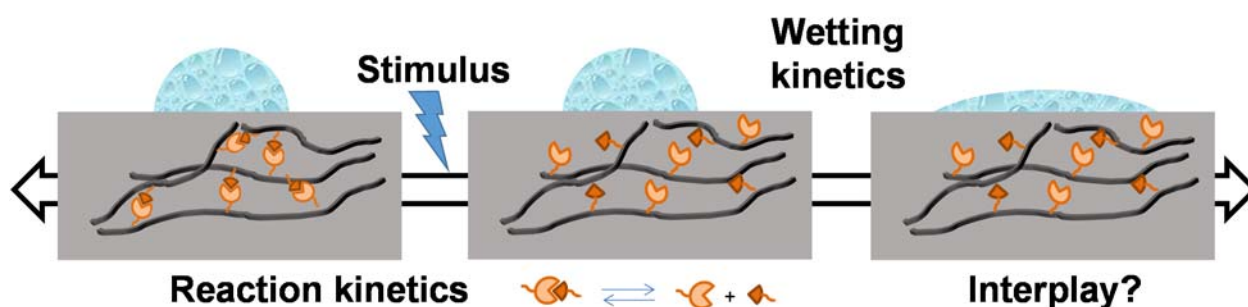


Figure 11: Schematic representation of time-dependency of the stimuli application and the resulting change of the interaction between the liquid and polymeric substrate. Within the project, the kinetics of both processes (reaction and wetting) will be elucidated in detail as well as independently from each other. Furthermore, the interplay between both will be studied.

The last point of interest within **WP4** is the stepwise addressability of the polymer (**Figure 12**). For this purpose, the mixed copolymers containing at least two different reversible groups will be utilized. The design of the copolymers will be designed based on the results obtained until this stage of the project. Thus, a very reversible moiety and a more stable one will be polymerized into one copolymer (**WP2**). Afterwards, a stimulus will be applied and the intensity of this stimulus will be increasing continuously. The interaction of the liquid and the solid phase will be monitored during this process and the successive progress of the change in the interaction will be monitored as function of time as well as stimulus intensity (pH-value, temperature). In this context, it is possible that two steps of switching will be observed or otherwise a continuous progress can be revealed. This behavior will be analyzed in detail within **WP4**.

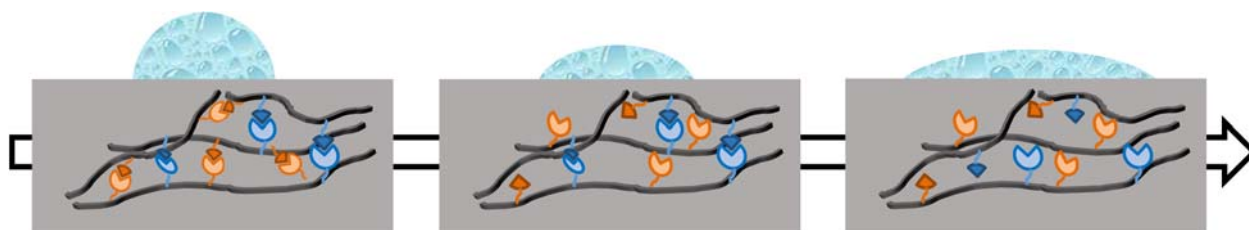


Figure 12: Schematic representation of the stepwise switching of the interaction of polymer substrate and a liquid. During constant increase of the stimulus intensity (decreasing pH-value or increasing temperature) from left to right, the interaction constantly changing.

Schedule of proposed work (dark: high workload, bright: low workload).

	Year 1		Year 2		Year 3	
	months 1-6	months 7-12	months 13-18	months 19-24	months 25-30	months 31-36
WP 1						
WP 2						
WP 3						
WP 4						

2.4 Data handling

All experimental lab work will be documented in laboratory journals, which will be stored centrally also after the conclusion of this research project. Data that will be generated will be saved not only on the working computers of the coworkers and the laboratory computers but also centrally on servers of the Jena Center for Soft Matter. Here they are protected from data loss by regular and routine back-up copies. Hence, the data and protocols of this project will be stored for at least ten years after completion of the project so that the raw data acquired can be made available upon request to complement the published data and graphs.

2.5 Other information

The Friedrich Schiller University Jena offers ideal requirements for the successful execution of the requested project. The Jena Center for Soft Matter (JCSM) provides excellent opportunities for cooperations, in particular for the characterization and analysis of the achieved materials. The applicants are both founding members of this center.

2.6 Descriptions of proposed investigations involving experiments on humans, human materials or animals

n/a

2.7 Information on scientific and financial involvement of international cooperation partners

n/a

2.8 Information on scientific cooperation within SPP 2171

The project will provide novel materials and characterization methods, which can also be utilized for the success of other projects within the SPP. Both PIs of the projects are highly motivated to cooperate with other projects in order to generate an additional benefit for both cooperation partners. We will provide the possibility to measure standard Raman spectroscopy as well as CARS microscopy for substrates available within the SPP (transfer of the measurement principle to other substrates). Furthermore, we are highly motivated to provide materials for other testing methods within the SPP in order to understand the wetting and dewetting behavior in more detail. All experimentally obtained results will also be provided in order to support projects using computational techniques.

In particular, it is planned to cooperate with Prof. Dr. Frank Müller (FSU Jena), who can provide laser ablation. This technique enables a nano-structuring of the surface providing the possibility to study the influence of structured surface of this new type of polymer substrate on the wetting behavior. Furthermore, we plan to cooperate with the group of Dr.-Ing. Michael Selzer (KIT). The data obtained from the contact angle measurements (e.g., surface tension) will be provided. Additionally, the information about the underlying kinetics revealed by CARS spectroscopy and contact angle investigations will also be utilized by Dr.-Ing. Michael Selzer to perform theoretical simulations on wetting phenomena. Consequently, a correlation of theoretical and experimental data will be accessible gaining a detailed understanding of the wetting behavior of our polymer systems.

Finally, the PIs will also provide hands-on tutorials for the central project of the SPP. Potential topics would be Raman and non-linear Raman spectroscopy for material characterization as well as synthetic topics like controlled radical polymerization, characterization of polymers (also specific topics in this context like differential scanning calorimetry or molar mass characterization). The final topics will be defined in cooperation within the complete SPP (in particular with the coordinator of the SPP).

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4 Requested modules/funds

4.1 Basic Module

4.1.1 Funding for Staff

FSU Jena – IOMC and IPC

1 Post-Doc, salary according to TV-L E13 (100%) – duration of employments: 36 months

The research of the proposed project will be covered by one (joined) Post-Doc position. This person (f/m) should feature expertise in synthesis as well as characterization of polymers and, furthermore, in spectroscopic analysis of materials. The Post-Doc will be employed at both groups (Dr. Hager and Prof. Popp). He or she will be responsible for the synthesis of the reversible monomers as well as the resulting polymer networks. The Post-Doc will perform the characterization of those materials using standard characterization techniques like NMR or SEC. Furthermore, he or she will perform the contact angle measurements as well as the CARS-spectroscopic analysis. Within this context, also time-dependent measurements as well as the imaging will be analysed in detail. Since the tasks are wide-spread between different disciplines, an experienced Post-Doc is required for the project.

In addition, student research assistants will assist the Post-Doc. For this purpose, two student research assistants are applied, each 9 months, 20 h per month and one starting at the 2nd half of the first year and the second one starting at 2nd half of the second year of the project. One student assists the work outlined under **WP1**. The other student assists the work outlined under **WP2**. They will perform the synthesis of the functionalized model systems and monomers and will further assist for the optimization of the polymer preparation. At FSU Jena the Organic Chemistry Lab Course' teaches experimental skills in the second year of chemistry studies. After that, even without B.Sc. degree, students are able to support the doctoral candidates in experimental work and they themselves benefit by gaining experience in scientific research.

Salary for students working on the project (20 h per month; 18 months; à 13.18 € per hour) €

4,744.80 €

Total:

4,744.80 €

4.1.2 Direct Project Costs

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

Chemicals for synthesis, solvents, glassware and other lab consumables are indispensable for macromolecular synthesis, preparation of films and samples.

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Chemicals (e.g., specialty chemicals, solvents, deuterated solvents for NMR spectroscopy)	4,000 €/a
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Consumables (e.g., silica for column chromatography, columns for flash chromatography, special glass ware, microwave vials)	2,000 €/a
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Optics and optomechanics (e.g., mirrors, polarizers, waveplates, lenses, notchfilters, mounts, filters, Raman compatible substrates)	7,000 €/a
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Equipment money 4.1.2.1 total:	13,000 €/a
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4.1.2.2 Travel Expenses

The active participation at scientific conferences will nurture both the presentation of the results obtained in this project and the discussion with international colleagues. The conferences listed below are highly relevant for discussion of the work proposed here. Additionally funding for the travel to the SPP meetings is requested.

Makromolekulares Kolloquium in Freiburg 2020	500 €
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2020 ACS National meeting	2,500 €
2020 ICORS Rome	1,500 €
SPP workshops 1 st and 2 nd year	1,500 €
Advanced school – SPP meeting 1 st year	500 €
PhD-candidate workshop – SPP meeting 2 nd year	500 €
International conference – SPP meeting 3 rd year	750 €
Travel money 4.1.2.2 total (3 years)	7,750 €

4.1.2.3 Visiting Researchers (excluding Mercator Fellows)

n/a

4.1.2.4 Expenses for Laboratory Animals

n/a

4.1.2.5 Other Costs

n/a

4.1.2.6 Project-related publication expenses

For publication in international double-peer review *open-access journals* we apply for 750 € per year.

Publication costs in total:

2,250 €

4.1.3 Instrumentation

n/a

4.1.3.1 Equipment exceeding Euro 10,000

n/a

4.1.3.2 Major Instrumentation exceeding Euro 50,000

n/a

4.2 Module Temporary Position for Funding

n/a

4.3 Module Replacement Funding

n/a

4.4 Module Temporary Clinician Substitute

n/a

4.5 Module Mercator Fellows

n/a

4.6 Module Workshop Funding

n/a

4.7 Module Public Relations Funding

n/a

5 Project requirements

5.1 Employment status information

Dr. Martin D. Hager permanent position at the Laboratory for Organic and Macromolecular Chemistry, Institute for Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena.

Prof. Dr. Jürgen Popp, Chair Physical Chemistry, Institute for Physical Chemistry (IPC), Friedrich Schiller University Jena and Scientific Director, Leibniz Institute of Photonic Technology Jena

5.2 First-time proposal data

n/a

5.3 Composition of the project group

The **research group of Martin D. Hager** at the Laboratory for Organic and Macromolecular Chemistry consists of five PhD students and two undergraduate students. The Post-Doc will directly work on the topic. In addition, it is intended that one Master student as well as research assistants will support the Post-Doc researcher for the synthetic part of the project.

The **research group of Prof. Dr. Jürgen Popp** at the Institute of Physical Chemistry and Leibniz Institute of Photonic Technology consists of 10 Post-Docs and research associates, 25 PhD students as well as several master and bachelor students. The Post-Doc will work on the

topic and it is intended that the research assistants will support him/her during the physical (characterization) part of the project. Here, the practical realization of the experimentally demanding CARS microscopy experiments and the realization of a combined CARS and critical angle setup will be assisted by apl. Prof. Dr. Michael Schmitt (research assistant at the chair of Prof. Popp with permanent position). Apl. Prof. Schmitt is an expert in non-linear Raman spectroscopy.

5.4 Cooperation with other researchers

n/a

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

n/a

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

Dr. Martin D. Hager performed substantial collaborative work with the following colleagues: Prof. Dr. Benjamin Dietzek (Leibniz-IPHT Jena), Prof. Dr. Leticia González (University Vienna, Austria), PD Dr. Harald Hoppe (FSU Jena), Prof. Dr. Stefan Hecht (Humboldt-University zu Berlin), Prof. Dr. Sybrand van der Zwaag (TU Delft), Prof. Dr. Ralf Weberskirch (TU Dortmund), Prof. Dr. Sven Rau (University Ulm), Dr. Santiago Garcia (TU Delft), Prof. Dr. Jean-Francois Gohy (Université catholique de Louvain), Prof. Dr. Wolfgang H. Binder (MLU Halle-Wittenberg), Prof. Dr. Frank Müller (FSU Jena), Prof. Dr. Matthew J. Harrington (McGill University Montréal), Prof. Dr. Boris Mizaikoff (Ulm University).

Prof. Dr. Jürgen Popp performed substantial collaborative work with the following colleagues: Prof. Dr. Volker Deckert (FSU Jena), Prof. Dr. Ulrich S. Schubert (FSU Jena), Prof. Dr. Stefanie Gräfe (FSU Jena), Prof. Dr. Benjamin Dietzek (Leibniz-IPHT), Prof. Dr. Francesco Pavone (LENS, Florence), Prof. Dr. Andreas Zumbusch (University Konstanz), Prof. Dr. Marcus Motzkus (University Heidelberg), Prof. Dr. Sebastian Schlücker (University Duisburg-Essen, Germany), Prof. Dr. Boris Mizaikoff (University Ulm), Prof. Dr. Sven Rau (University Ulm).

5.5 Scientific equipment

The **group of Dr. Martin D. Hager** has the required lab workplace at the Laboratory for Organic and Macromolecular Chemistry. Moreover, the required equipment for the characterization of the synthesized materials is accessible (Laboratory for Organic and Macromolecular Chemistry - Prof. Dr. Ulrich S. Schubert): Size exclusion chromatography to determine the molar masses of the polymers, elemental analysis and NMR spectroscopy (solution as well as solid state) to analyze the structure of the monomers and the materials as well as composition of the polymers, UV-vis spectroscopy (solution, film), mass spectrometry (ESI-MS and MALDI-TOF MS) and differential scanning calorimetry (DSC) as well as thermogravimetry (TGA) for the analysis of the thermal properties of monomers and polymers. Most importantly, contact angle measurements (OCA 30 from Dataphysics) can be performed and the polymer films can be investigated (in collaboration within the IOMC) with confocal laser scanning microscopy (CLSM). The group of **Prof. Dr. Jürgen Popp** has multiple linear and non-linear Raman, fluorescence- and UV/Vis- as well as IR-absorption setups available. The experimental setups allow for routine recording of Raman spectra with excitation wavelengths ranging from 300 to 1064 nm. Furthermore, several highly flexible non-linear Raman (*i.e.* CARS) imaging setups, *i.e.* laser scanning microscopes equipped with tunable ultrafast laser sources (tuning-range 500 – 3300 cm⁻¹) are available. Among those, there are home-build, compact and portable setups, which can be used for combination with contact angle measurements. All these setups can be used without any restrictions for the work proposed here.

5.6 Project-relevant cooperation with commercial enterprises

n/a

5.7 Project-relevant participation in commercial enterprises

n/a

6 n/a Additional information

n/a