DoDyNet - Workpackage 1 – Deliverable 1.22 Number 103 :

Management Report – Year 1

1. General progress of the action

General objective

Polymer gels and networks are fascinating versatile soft materials which are ubiquitous in daily life (foodstuff, cosmetics) and high-added value applications (tissue engineering, sensors, drug storage and delivery, portable batteries[1]), and can exhibit both solid-like and liquid-like properties. Classical methods of crosslinking these networks fall into two categories, chemical and physical, and the properties of the respective networks generally encompass two extreme cases: (i) Permanent networks, covalently crosslinked, able to resist flow and creep, and to swell without losing their coherence, but with limitations in terms of their processing and recycling. (ii) Physical networks, which are reversible, easily processable and recyclable, but creep at long times and show residual deformations in loading/unloading cycles. **Today, the biggest challenge with this important class of responsive materials is to efficiently combine and control within the same material all distinct features that make them ideal for applications, such as high mechanical strength, large reversible deformability in shear and extension, substantial reversible swelling, and self-healing properties.** It is important to transfer the knowledge acquired from bulk networks (elastomers) to the properties of solvent-mediated swollen gels. This has emerged as a priority theme for the development of so-called smart (i.e., multiply responsive) materials.

Within DoDyNet, we would like to address this challenge, inspired by the recent progress made in this field, reached thanks to the development of **new types of polymer networks:** While different, these new materials **share a common concept**, which is the **combination of at least two distinct dynamic modes** within the same material in order to display multiscale viscoelastic responses under the influence of an external stress or deformation field. Consequently, they are characterized by a **'double' mechanical behavior**, which offers a better balance between the desired properties.

Therefore, we would like to design, synthesize and characterize new double polymer networks, which will allow us to investigate and understand how to control their dynamics by playing with their composition. Based on these results, we would like to develop models to relate the properties of these polymer networks and their architecture. Such fundamental understanding will help us to answer the requests from our industrial partners about developing new materials based on this strategy.

[1] (a) Peppas, N., J. J., Sahlin, Biomaterials **1996**, 17, 1553; (b) E.S. Seiffert, Adv. Polym. Sci. **2015**, 268; (c) Wolff, L., K. Kroy, Phys.,Rev. E **2012**, 86(4), 040901.

Methodology

In order to accomplish our objectives, the institutions in DoDyNet have been chosen in order to cover, all together, the necessary expertise for the project, i.e. a **strong expertise in synthesizing responsive networks, the use of many state-of-the art (home-made) measurement techniques, most accurate models, detailed questions and advices from major companies, and large support of visiting experts**.

Before starting the project, during the elaboration of the proposal, we have designed new DDNs which fulfill the criteria that we believe are important in order to obtain polymer networks with novel properties (see Section 1.1.3 of the project). They consist in three main categories of samples:

1) Model systems based on a combination of metal-ligand interactions, phase separation and entanglements

2) DDNs based on reversible covalent bonding

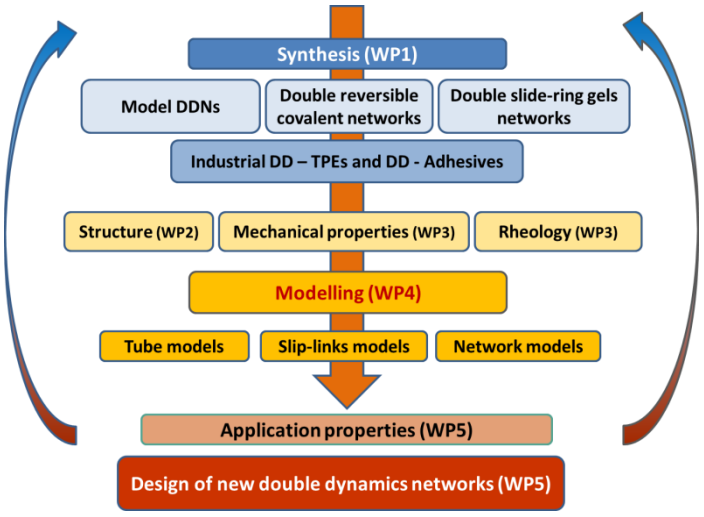
3) slide-ring gels.

In parallel, two classes of industrial samples have been also proposed, in concertation with our industrial partners:

4) Double Dynamics Thermoplastic elastomers

5) Pressure sensitive adhesive (PSA) DDNs

The synthesis and characterization of these different samples represent a large part of our project. The research competences have been organized in several work packages (WPs):



WP1 – Synthesis: Our project requires the synthesis of different Double Dynamic Networks (DDNs), which will serve to develop a deep conceptual understanding of the dynamics and mechanical properties of DDN, as well as to create novel DDNs.

WP2 – Structure: The development of new DDNs with improved mechanical properties relies on polymer-network topologies and architectures and mandates a structural characterization on multiple length scales (from 1 to 10^3 nm).

WP3 – Dynamics and rheology: Investigation of DDNs properties with special attention to diffusion, rheology and mechanical response as functions of entanglements, composition and chain architecture. In order to develop a general picture, these studies will be complemented by analysis of the elasto-capillary effects in these DDNs.

WP4 – Modelling: Experimental results shall feed two different models at both mesoscopic and atomistic levels. These models will be validated and form the basis for designing new systems of interest.

WP5 – Application properties and product design: The results of WP1 – WP4 will be combined in order to assess the role of molecular structure of DDNs on their application properties. This will yield design criteria for polymeric structures with desired performance. The tasks are (i) identify the relevant properties for the target industrial applications, (ii) determine the structure and composition of specific DDNs in order to obtain these properties, (iii) select the appropriate synthesis scheme in order to produce such DDNs in large amount, and (iv) test and validate these ideas and concepts. We will also study specific samples already available from Partner P8 and P9 and propose modification to improve their properties.

Main results obtained so far (up to April 2019)

So far, the project is progressing well, with no large deviations compared to the proposal. The synthesis first samples have been shared among the different partners. Besides the synthesis, the structure and dynamics of the different samples are presently characterized, in order to build global understanding of their behavior. We are therefore at the stage where we collect results for the different systems and try to make links between them.

So far, model systems which have been synthesized and which are available for the network are:

1) Metallo-supramolecular star polymers: PnBA-based stars polymers have been synthesized by ESR1. They are presently analyzed by ESR5 who is studying their flow dynamics under large shear deformation, and ESR12 who is investigating the influence of using two different ions into the same sample, in order to have two different lifetimes of the reversible bonds and reach a double dynamics. ESR12 is now developing a mesoscopic model to describe the linear viscoelastic properties of these systems.

In parallel, ESR10 has synthesized PEO-based star polymers bearing one or two different functional groups at their extremities, in order to allow one or two different kinds of reversible interactions.

Future plans: ESR12 will collaborate with ESR5 and ESR6, in order to investigate the same systems under nonlinear shear and extensional flow. ESR10 will investigate the structure and diffusion in the PEO-based DDNs. All the results will be shared in order to work on developing a global picture to explain the properties of telechelic star polymers.

2) Polymer networks from ABA triblock copolymers: ESR1 is synthesizing triblock copolymers of different compositions in order to obtain a polymer network based on phase separation process. The first samples have been analyzed by ESR8 under linear and nonlinear shear rheology. In parallel, ESR3 has synthesized supramolecular tri-block copolymers.

Future plans: improving the synthesis to reach a stronger phase separation. In a second step, systems 1) and 2) will be blended. The copolymers synthesized by ESR3 still need to be characterized.

3) Unentangled sticky chains: ESR11 has developed a model to describe the dynamics of unentangled sticky chains. In parallel, ESR1 has synthesized such materials, which will allow validating the model of ESR11.

Future plans: The model of ESR11 will help designing new systems suitable with the synthesis protocol of ESR1, with specific properties. In a second step, ESR11 will add covalent bonds to this reversible networks, in order to investigate DDNs similar to the dual polymer networks provided by tesa.

4) Dual polymer networks: ESR8 is presently studying the viscoelastic properties of the dual polymer networks provided by tesa for adhesive applications. The objective is to understand what is the specific role of both the covalent and reversible bonds, and how their properties depend on the lifetime of the metal-ligand interactions.

Future plans: Modelling of such complex system is required in order to rationalize the influence of the different parameters (branching density, lifetime of the reversible bonds, concentration, molar mass of the chains,…). This will be achieved by ESR11 (at a detailed length scale) and by UCL team (at a more coarse-grained length scale).

5) Entangled sticky chains: ESR6 has studied the extensional properties of entangled sticky PS chains, and have started investigating the properties of PS ionomers. She has shown how the presence of hydrogen bonds can strongly enhance the ductility of the sample.

Future plans: similar measurement protocol will be applied to other samples provided by the network, in order to understand their stretching behavior.

6) Thermoplastic elastomers: ESR9 has studied the morphology and the rheological and mechanical properties of specific thermoplastic elastomers synthesized by the industrial partner DSM, in order to understand the role played by the chain length and the density of the associating hard segments and improve their properties. In collaboration with UCL, he has developed statistical tool in order to better describe the composition of such samples.

Future plans: the molecular picture developed by ESR9 will be tested on other sticky polymers, such as the ones of ESR6, in order to develop a general framework to analyze such sticky materials.

7) Synthesis of slide ring gels: ESR2 has determined a proper protocol to synthesize slide-ring gels based on polyrotaxane. First gels are now available and their corresponding rheology results are promising.

Future plans: ESR2 has to play with the gel composition in order to obtain the best properties in term of extensibility and elasticity. These gels will then be shared to the network for further investigation. In particular, soft slide-ring gels will be sent to ESR7 in order to determine their elasto-capillary properties, based on the protocol she has developed to study the properties of telechelic polymers.

8) Synthesis of model thermoplastic elastomers based on dynamic covalent bonds: ESR3 is working on the synthesis of different polymer networks based on dynamic covalent bonds based on two different crosslinking functions in order to create interpenetrated networks. So far, the precursors have been developed and first cross-linking experiments were successful.

Future plans: The first samples are nearly ready to be distributed to the DoDyNet partners for more characterization. In particular, ESR10 will use a combination of diffusion techniques in order to investigate the sample structure at the different length scales. The synthesis scheme developed here can easily be adapted for the design and creation of new double networks.

9) Microgels formed by attractive soft colloidal particles: These gels, which are based on polyelectrolytes, have been prepared by ESR4, who has also studied their rheological behavior. These materials have shown interesting aging properties.

Future plans: It would be very interesting to understand how this system breaks under sample elongation. To this end, it is planned to use the diffusive wave spectroscopy setup which is presently developed by ESR13 in order to follow the dynamics and structure of a

polymer network during fracture. Light scattering will also be performed, in collaboration with FORTH.

Another perspective is to couple this synthesis scheme with the one of UCL (based on metal-ligand interactions) in order to develop novel sticky microgels.

2. Mid-Term Check Progress Report on ESR individual work (up to April 2019)

ESR 1 Clément Coutouly

Synthesis and Dynamics of model supramolecular polymer networks
Institution: UCL
Supervisors : Charles-André Fustin, Evelyne van Ruymbeke
Period covered : 05/03/2018 to 29/04/2019

The objective is to synthesize and study the dynamics of model fully supramolecular double networks. They are based on a combination of metal-ligand interactions, phase separation and entanglements. The first, long life time, network is made from ABA triblock copolymers with a long central block and small outer blocks to ensure phase separation with strong and stable association. The second, short life time, network is built from telechelic stars or long linear polymers bearing terpyridine ligands at the chain-ends or along the chain, and crosslinked by the addition of transition metal cations. Here, we report on the synthesis of the ligand-functionalized and ABA triblock polymers by RAFT polymerization, and on the characterization of the two individual networks to fully understand the influence of the tailored bonds in the networks. These systems were studied by linear rheology in melt as well as in the solution according to different parameters such as composition, molar mass, ligand density, block length, nature of solvent.

So far, ABA triblocks with different composition and different molar mass have been synthesized. The block A is made of polystyrene (PS) with a total molar mass which is between 2 400 g/mol and 23 800 g/mol. This allows to form Block copolymer with different length. With the same idea, several poly n-butylacrylate (PnBA) with different molar mass have been synthesized using PS macro Raft agent. These systems have been studied by Linear Rheology in melt and also in solution with Isopropanol. This system is still studied.

Moreover, other ABA triblocks have been developed to be studied in aqueous solutions. There are made of PnBA as outer hydrophobic Block and Polydimethyacrylamide (PDMA) as center hydrophilic block. This system is synthesized by RAFT polymerization and studied in solution by Linear Rheology.

Therefore, long linear polymers bearing terpyridine along the chain have been synthesized. Their molar mass is closed to ABA triblocks. The system studied is composed of 4 terpyridine per chain. Rheology in melt without metal first and then by introducing 0.5 equivalent of metals have been used to characterize them (0.5 eq means we are introducing the stoichiometry according to terpyridine to form bis-complex).

ESR 2 Rowanne Lyons

Institution: UCL

Supervisors: Charles-André Fustin, Evelyne Van Ruymbeke

Period covered: 15/09/2018 to 30/04/2019

Objectives of Research

- To design new soft functional materials with improved properties based on the central concepts of double dynamics and slide-ring gels. These properties include being easy to process and recycle, resistance to flow and creep, the ability to dissipate energy to resist fracture, a high equilibrium modulus and double network properties in melt and in solution
- To characterize the double dynamic networks by linear and non-linear rheology

Methodology

1. Synthesis of first network of polymers crosslinked by metal-ligand bonds
2. Synthesis of second network based on slide-ring gels
3. Synthesis of optimized double network by variation of amount of metal-ligand precursors, lifetime of the metal-ligand, amount of polyrotaxane crosslinker and preparation conditions
4. Characterisation of double network by linear and non-linear rheology

Achievements

Creation of second network (slide ring gel):

- Synthesis and characterisation of polyrotaxane and polyrotaxane crosslinker
- Variation of chemical properties of polyrotaxanes: functionality, degree of functionalisation
- Preparation of gels of varying compositions according to the amount of crosslinker and the type of crosslinker
- Preliminary linear rheological analyses of the second network

ESR 2 Larissa Hammer

Design and Characterization of Novel Double Dynamic Networks (DDNs) Based on Reversible Covalent Bonds

Institution: ESPCI

Supervisor: Renaud Nicolaÿ

Period covered: 04/06/2018 to 30/04/2019

List of Abbreviations

ATRP atom-transfer radical polymerization
CTA chain transfer agent
Đ polydispersity index
DDN double dynamic network
DN double network
DPn number-average degree of polymerization
FRP free radical polymerization
IR infrared
Mn number average molecular weight
MMA methyl methacrylate
nBA n-butyl acrylate
NMP nitroxide-mediated polymerization
NMR nuclear magnetic resonance
PBA phenylboronic acid
P(nBA) poly(n-butyl acrylate)
RAFT reversible addition - fragmentation chain transfer
SEC size exclusion chromatography
SN single network
Tg glass transition temperature
UV ultraviolet
Vis visible

Introduction

A polymer network is a system consisting of cross-linked polymer chains. The cross-links can be of different nature and determine the characteristics of the material. Permanent cross-links allow the system to be creep and flow resistant, give enhanced mechanical strength and allow the material to swell without any loss in coherence. The downside of permanent cross-links is that they don't allow the material to be reprocessed or recycled.

In contrast to that, non-permanent cross-links allow the material to be reprocessed or recycled. However, the unsteadiness of the cross-links leads to creep and limited mechanical properties. The ideal case would be a material that allows the combination of distinct features of both materials.

So called double dynamic networks (DDNs) are polymer networks that combine at least two distinct dynamic modes. This leads to a double mechanical behavior. As for the nature of these dynamic modes the toolbox of chemistry provides a wide range of possibilities. Cross-links can consist either of chemical (covalent) bonds or physical interactions. Examples for physical interactions are: ionic bonds, hydrogen bonds, hydrophobic interactions (micell formation, microseperation...), π – π stacking, or metal-ligand coordination.

Chemical bonds are commonly permanent covalent bonds. However, some particular covalent bonds are reversible and thus can be also non-permanent. Reactions that can be used to form such bonds are diverse and can be placed in two categories: reactions that proceed via a dissociative mechanism (reversible cross-links) and reactions that proceed via an associative mechanism (dynamic cross-links). In the first case, the bonds that have been formed by two reaction partners have to be broken first before elsewhere a new bond can be formed, in the latter case the original cross-link can only be broken if the new reaction partner is actively involved in the reaction. Hence, a network built up by dynamic bonds has always the same amount of cross-links. This gives the material properties like self-healing, reprocessability, and malleability while simultaneously maintaining the networks integrity and toughness.

As a synthetic polymer chemist my part of the DoDyNet project is to design and synthesize novel DDNs and to do some basic characterization. I will use my laboratories expertise to employ dynamic covalent bonds in DDNs. At the moment I am working on two different projects I want to present individually: In the first and main project ’Double

Networks’ I want to synthesize double networks with two different kinds of dynamic cross-links. The second project ’Thermoplastic Elastomers’ is a cooperation with the University of Mainz and focuses on the employment of dynamic covalent bonds in thermoplastic elastomers.

Project Double Networks

This project represents the main focus of my work so far. The general aim of this project is to design and synthesize polymer networks with at least two different kinds of crosslinkers.

This would allow the tailoring of outstanding materials displaying properties such as responsiveness, self-healing, shape memory, creep resistance, fatigue resistance, and mechanical strength.

The two cross-linkers can be incorporated in the network in two different ways. Either the network consists of only a single network (SN) where both cross-linkers are incorporated in the same polymer or it is composed of two independent, interpenetrating networks, each cross-linked with one respective cross-linker to form a (interpenetrated) double network (DN). In our first experiments we decided to focus on the synthesis of DNs. DNs can be synthesized via different strategies. Generally, they are synthesized by a sequential

procedure, first building one network, swelling it with a solvent and then subsequently synthesizing the second one inside the first one.1 This procedure has three drawbacks: The network first synthesized has to swell very efficiently to guarantee a homogenous interpenetration of the two networks, the network formation can hardly occur in a controlled manner and in addition to that the chemical analysis of the structure in an already cross-linked material is challenging. Therefore, the general approach in this project is to synthesize the DDNs via the cross-linking of two different functional thermoplastics.

Thermoplastics are linear polymers that can be precisely tailored (if needed) by specific polymerization methods such as atom-transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible addition - fragmentation chain transfer (RAFT) polymerization. Thus, it is possible to precisely control their length and functional density (and in consequence the cross-linking density). Additionally, thermoplastics can be easily analyzed via nuclear magnetic resonance (NMR) spectroscopy and other chemical analytic methods that would not be applicable to already cross-linked materials. Thermoplastics are in contrast to networks soluble in suitable solvents allowing the cross-linking to be conducted in solution, maintaining a homogenous distribution of the two different thermoplastics. The cross-linking is conducted by adding a difunctional small molecule to the functional thermoplastics like depicted in Figure 2.1.

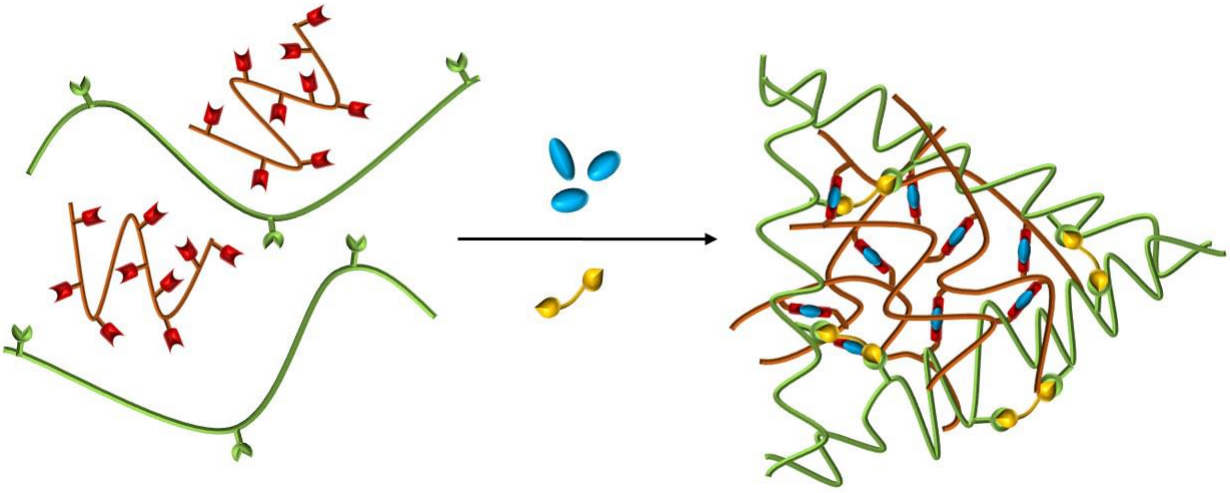


Figure 2.1: Concept of the cross-linking process to create a DDN. The two networks are cross-linked simultaneously by employing two different functional thermoplastics. The cross-linking takes place by adding difunctional small molecules that react with the respective functional groups of the thermoplastics orthogonally.

The functional groups attached to the thermoplastics and the employed cross-linkers have to fulfill the following criteria: the cross-linking has to occur strictly orthogonal to maintain the independence of the two networks. In addition to that, the cross-linking has to be very efficient and go to high yields to control the cross-linking density. In an ideal case the cross-linking takes place without the addition of external catalysts or the formation of unwanted side products to guarantee a simple manufacturing process.

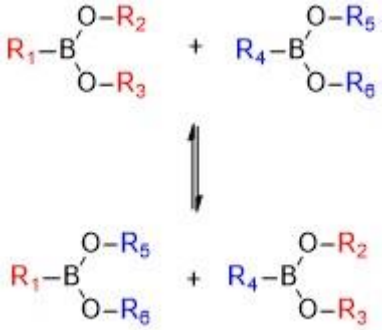
Small volatile side products could be removed by evaporation. There are only a few chemical reactions that fulfill these criteria.

Networks 1

Concept

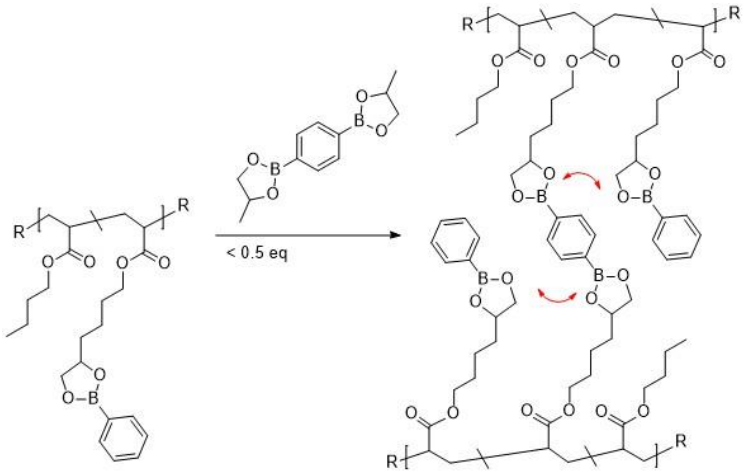
The first network of the interpenetrating DN (Network 1) should show a certain dynamic and is therefore tightly cross-linked. The aimed number average molecular weight (Mn) for the thermoplastics forming this network is around 100 000 Da (number-average degree of polymerization (DPn) 1000). The functional density is 100 cross-linking points per chain, which translates into 10% functionality. The cross-links have to be dynamic enough to participate in fast exchange reactions to dissipate energy and to undergo self-healing. The boronic ester/diol exchange is a very fast dynamic transesterification reaction leading to dynamic covalent bonds.2–6 The reaction can take place either between a boronic ester and a diol (transesterification) (Scheme 2.1) or two boronic esters (metathesis) (Scheme 2.2). The first reaction is very fast, the second one is tunable in its reactivity.6 The addition of water or diols catalyzes the reaction between two boronic esters and leads to a significant acceleration of the reaction. In absence of these catalysts the reaction hardly takes place at room temperature.

Scheme 2.1: Exchange reaction between a boronic ester and a diol.



Scheme 2.2: Exchange reaction between two boronic esters.

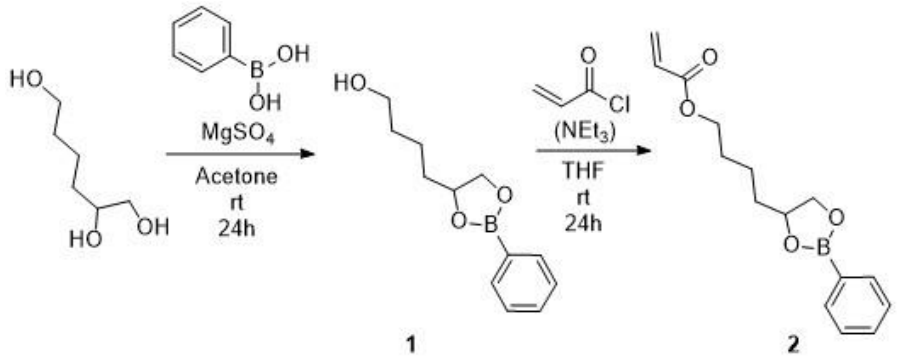
The DDNs should be readily applicable at room temperature. Therefore, the glass transition temperature (Tg) of the employes polymers has to be significantly below room temperature. The acrylate monomer n-butyl acrylate (nBA) is commercially available and cheap. It polymerizes to poly(n-butyl acrylate) (P(nBA)), a polymer with the linear formula of (C7H12O2)n and a Tg of -49_C. The general plan for the synthesis of Network 1 is to first synthesize boronic ester functional thermoplastics based on a nBA backbone and then cross-link it (simultaneously with Network 2) with a diboronic ester like depicted in Scheme 2.3.



Scheme 2.3: Cross-linking concept of the boronic ester-functional thermoplastics of Network 1

Results

To synthesize the thermoplastics that form Network 1 an acrylate monomer with a corresponding pending functionality has to be synthesized. It was attempted to synthesize a monomer carrying a phenylboronic ester group . A very straight forward way to do so is to start with the esterification of 1,2,6-hexanetriol with phenylboronic acid (PBA) to yield product **1** and the subsequent reaction of the remaining alcohol function with acryloyl chloride like depicted in Scheme 2.4. However, the phenylboronic ester group is very susceptible to water. Which made a isolation of the final monomer **2** impossible since it requires an aqueous work up.



Scheme 2.4: Synthesis of acrylate monomer **2** with a pending boronic ester functionality.

As an alternative reaction route, 1,2,6-hexanetriol can be protected via an acetal, a protecting group significantly more stable towards hydrolysis than PBA, to yield compound **3**. The protection was conducted by a reaction of the triol with acetone, which is additionally also cheaper than PBA. After the protection of the diol, the remaining hydroxyl group was esterified with acryloyl chloride. The resulting acrylic monomer **4** (Scheme 2.5) could be purified and is obtained in good yields.

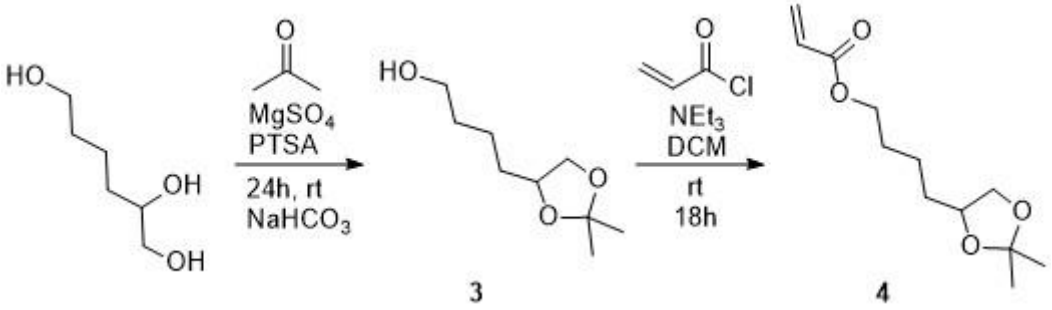
It was decided to deprotect the diol after polymerization to avoid a premature polymerization of the unprotected monomer. The polymerization was conducted via a RAFT mechanism like depicted in Scheme 2.6 to obtain well defined, linear polymer chains.

The polymerization of Polymer **P5** was conducted several times in a reproducible manner.

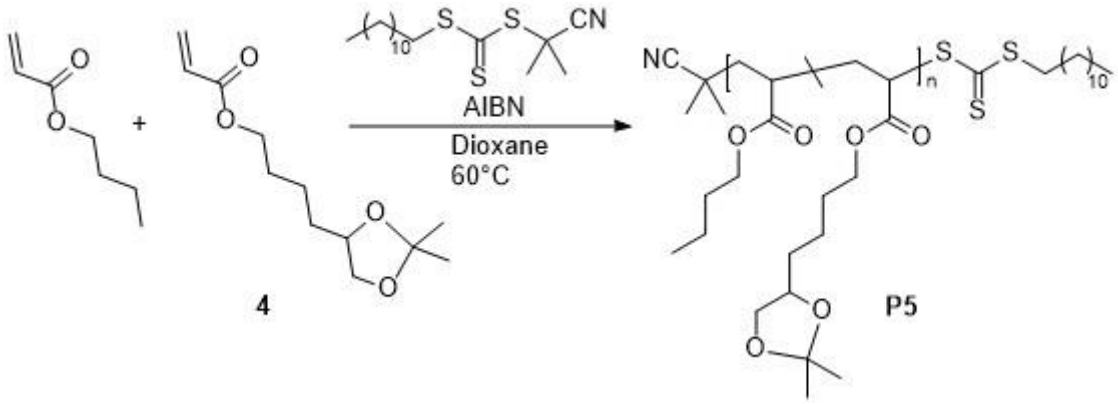
The polymer was obtained as a viscous, transparent yellow liquid with a Mn about

80 000 Da and a polydispersity index (Đ) about 1.3. The ratio of the functional monomer is around 10% and corresponds to the monomer feed. The monomer conversion was assessed via NMR spectroscopy right after the polymerization was stopped and was calculated to be 95%.

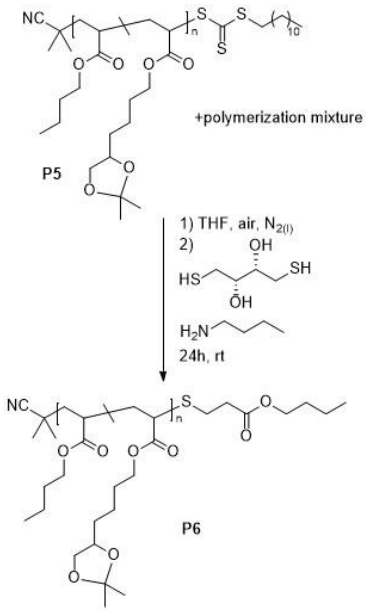
The RAFT end group of the resulting polymer causes the material to have a strong yellow color. Depending on the application field it would be more preferable to have a colorless polymer. In addition, the RAFT end group might cause some unwanted side reactions in the following reaction steps. Therefore, the RAFT end group has to be removed. This was achieved via an one pot aminolysis with a subsequent Michael addition like shown in Scheme 2.7.



Scheme 2.5: Synthesis of monomer **4** with a pending diol protected by an acetal group.

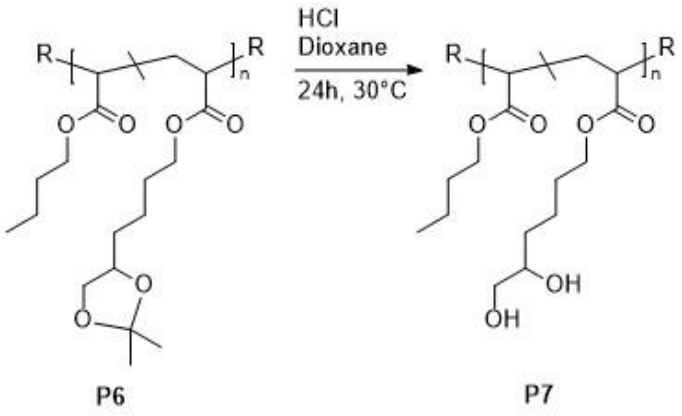


Scheme 2.6: RAFT copolymerization of nBA with the protected diol functional monomer **4** yielding polymer **P5**.



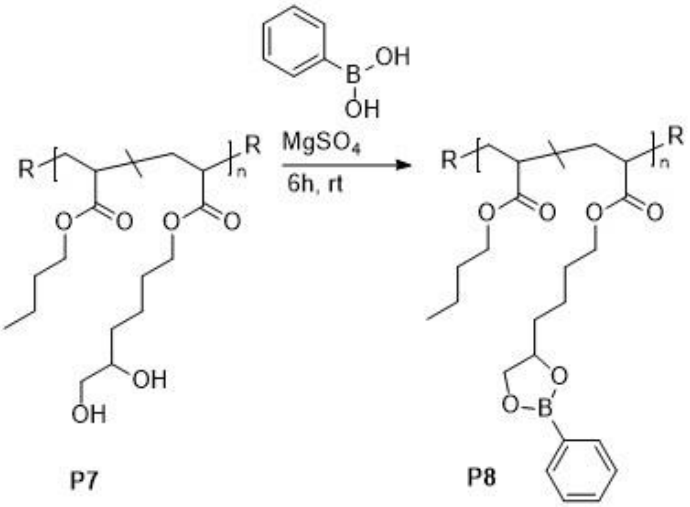
Scheme 2.7: RAFT end group transformation of **P5** using aminolysis with a subsequent Michael-addition to yield **P6**.

The subsequent deprotection of the diol groups in **P6** was conducted employing diluted and concentrated HCl in dioxane like shown in Scheme 2.8. **P7** was obtained as yellow-ish, transparent viscous liquid.



Scheme 2.8: Deprotection of copolymer **P6** using HCl in dioxane to yield **P7**.

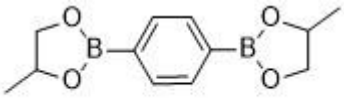
The next step was the reprotection of the polymer **P7** with phenyl boronic acid to yield **P8** like shown in Scheme 2.9.



Scheme 2.9: Reprotectiong copolymer **P7** with a boronic acid to yield **P8**.

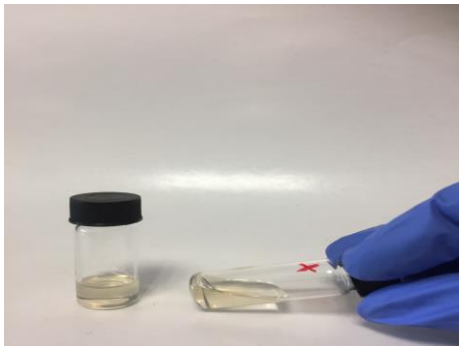
To conduct a first qualitative cross-linking test a solution of **P8** in THF was prepared and transferred in a small vial as shown in Figure 2.2. An identical second vial was prepared as a negative reference. A solution of a difunctional boronic ester cross-linker **9** (see

Scheme 2.10) was added to the first vial and an equal amount of pure THF was added to the reference vial. The amount of cross-linker was calculated to match 20% of the functional groups present in the sample. After 60 minutes the sample with the crosslinker has turned into a gel whereas the reference sample was still a liquid. This is a first qualitative proof that the reaction as envisioned in Scheme 2.3 works.

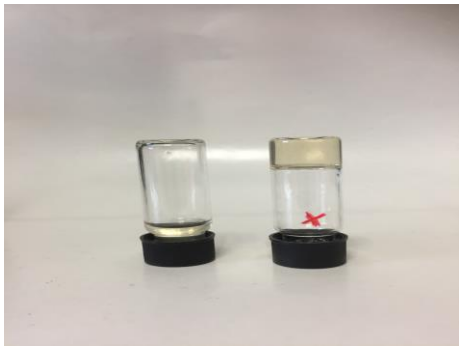


9

Scheme 2.10: Difunctional boronic ester cross-linker **9**.



(a) Before cross-linking.



(b) After cross-linking.

Figure 2.2: Qualitative cross-linking test: In Figure 2.2a two identical solutions of **P8** in

THF can be seen. Both solutions are liquid and flow when the vials are turned. To one sample (red cross, right) a cross-linking agent solution was added whereas to the reference sample (left) only pure THF was added.

Figure 2.2b shows the samples 1 h after the addition. The sample with the cross-linking agent has turned to a gel that doesn't flow, while the reference sample is still liquid.

Network 2

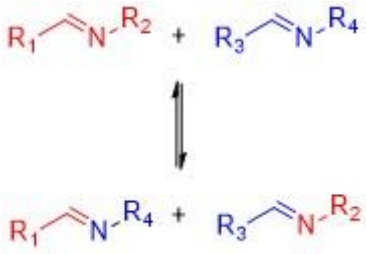
Concept

The second network is slightly cross-linked and needs therefore a relatively high molecular weight. Also here the system is based on P(nBA) to maintain a low Tg. The aimed

Mn for the thermoplastics of Network 2 should be around 500 kDa. The functional density aims for 10 cross-linking points per chain, which translates into 0.2% functionality.

The idea is to employ a second kind of dynamic cross-linker in this network to add a second dynamic mode to the DN. It should although be less dynamic than the system of the first network. For this cause a system consisting of aldehyde and imines can be employed. Aldehydes react with primary amines to imines. These imines can undergo exchange reactions ether with aldehydes (Scheme 2.11) or with other imines, catalyzed by aldehydes (metathesis) (Scheme 2.12).

Scheme 2.11: Exchange reaction between an aldehyde and an imine.



Scheme 2.12: Exchange reaction between two imines.

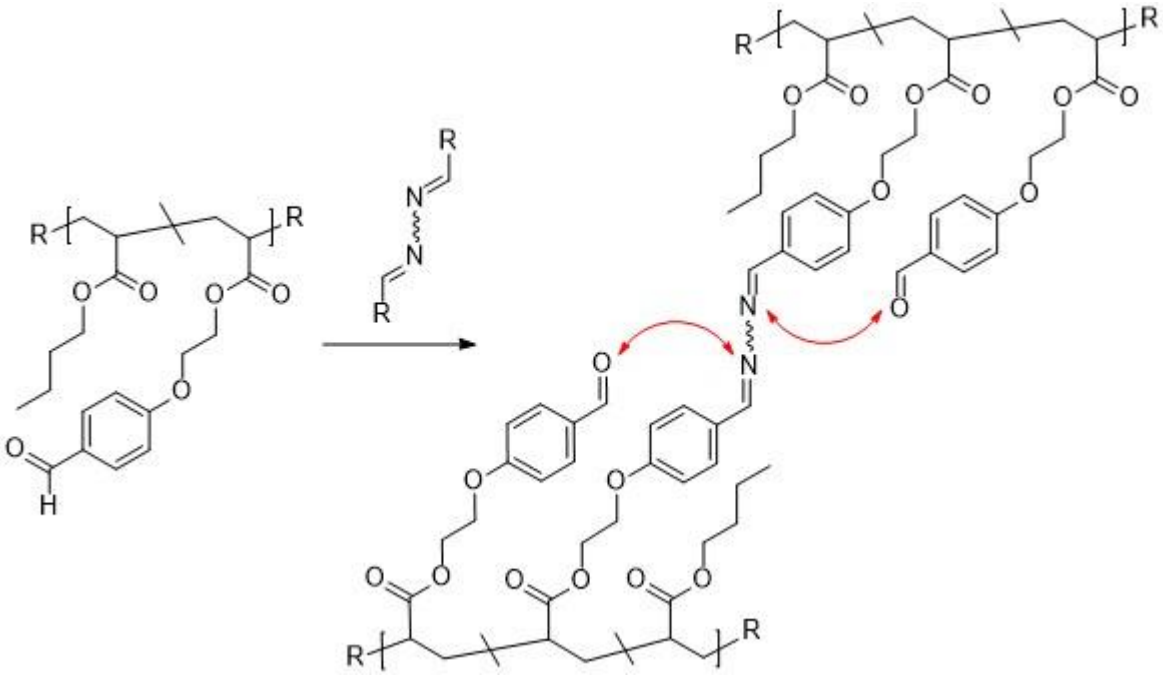
So an aldehyde functional thermoplastic can easily be cross-linked by a diimine like depicted in Scheme 2.13. The amount of still free aldehyde in the network determines the dynamic of the system.

Results

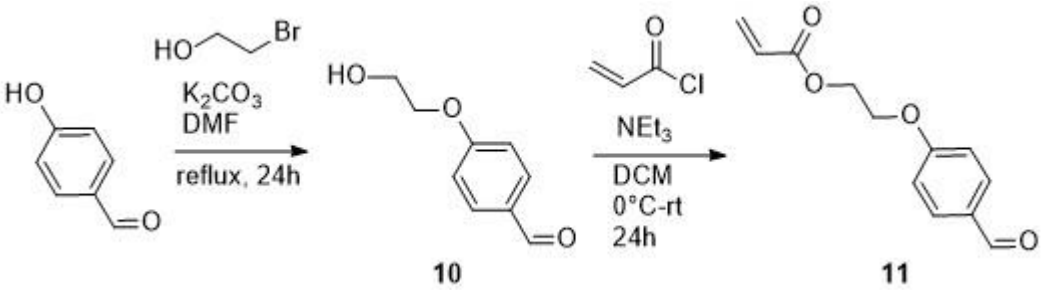
For the aldehyde/imine exchange system, a thermoplastic with pending aldehyde functionalities has to be synthesized. Therefore, a two step monomer synthesis like shown in Scheme 2.14 was developed according to a literature procedure.8 In the first step, 4-

hydroxybenzaldehyde was reacted with 2-bromoethanol to compound **10**. Subsequently, the product **10** was converted with acryloyl chloride to form the acrylate monomer **11**.

This route of synthesis works, but the product can only be obtained in low yields and with time consuming purification.



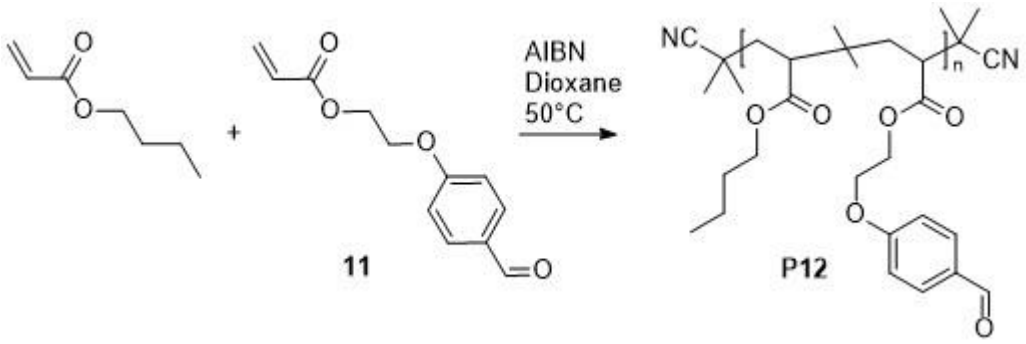
Scheme 2.13: Cross-linking concept of the aldehyde-functional thermoplastics of Network 2 via an imine exchange reaction. The network is dynamic in the presence of free aldehydes.



Scheme 2.14: Synthesis of acrylate monomer **11** with a pending aldehyde group.

The functional aldehyde monomer **11** was used in a copolymerization with nBA. Regarding the molecular weight of the polymer there was threshold around 300 kDa, a higher

Mn could not be achieved. Even with RAFT polymerization a controlled polymerization could only be maintained up to 200 kDa. It was therefore decided to conduct the polymerization via free radical polymerization (FRP) like depicted in Scheme 2.15, because of its undemanding reaction conditions. A Mn of 293 kDa and a Đ of 2.16 could be achieved.



Scheme 2.15: Free radical copolymerization of nBA with the functional aldehyde monomer **11** yielding polymer **P12**.

Outlook

The thermoplastic precursors for the DN have been successfully synthesized as well as the small molecule cross-linkers. First cross-linking experiments with one of the ther-moplastics have been conducted. The next step is to quantitatively validate the crosslinking using infrared (IR)-spectroscopy and/or rheology. Then the double network can be created. Once the double network is formed, mechanical and chemical tests can be performed (tensile test, swelling tests...). It can be also be distributed to other members of the project.

On a long time scale, the already achieved know-how can be used to create other DDN. It can be attempted to combine both cross-linking methods in a SN and compare it to the respective DN. Another idea is to employ also permanent cross-links alongside with the dynamic ones.

Thermoplatic Elastomers

The goal of this project is to synthesize thermoplastic elastomers employing dynamic covalent bonds. The elastomers are composed of linear A-B-A triblock co-polymers with ’hard’ outer blocks and a ’soft’ inner block like shown in Figure 3.1. Due to micro phase separation the outer blocks form crystalline domains that work as physical cross-links. The outer blocks are additionally connected by dynamic covalent crosslinks.

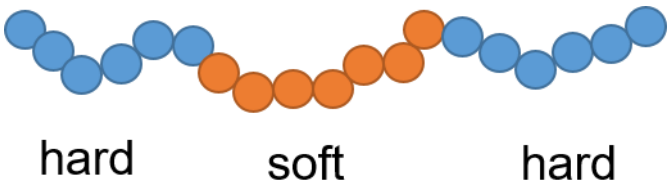


Figure 3.1: A-B-A triblock co-polymers with ’hard’ outer blocks and a ’soft’ inner block.

For this system the same chemistry should be applied that was already presented in Scheme 2.2. This gives the system two distinct dynamic modes: one below the Tg of the hard phase and one above it. In contrast to conventional thermoplastic elastomers this new system retains its network structure above the Tg due to the dynamic covalent bonds. The concept of this dynamic covalent thermoplastic elastomer is depicted in Figure 3.2.

Results

To obtain a well defined A-B-A triblock co-polymer RAFT polymerization has to be conducted employing a suited symmetrical chain transfer agent (CTA). The plan is to use a CTA whose Z-group is on the respective outside and the R-group is on the inside like shown in Scheme 3.1.

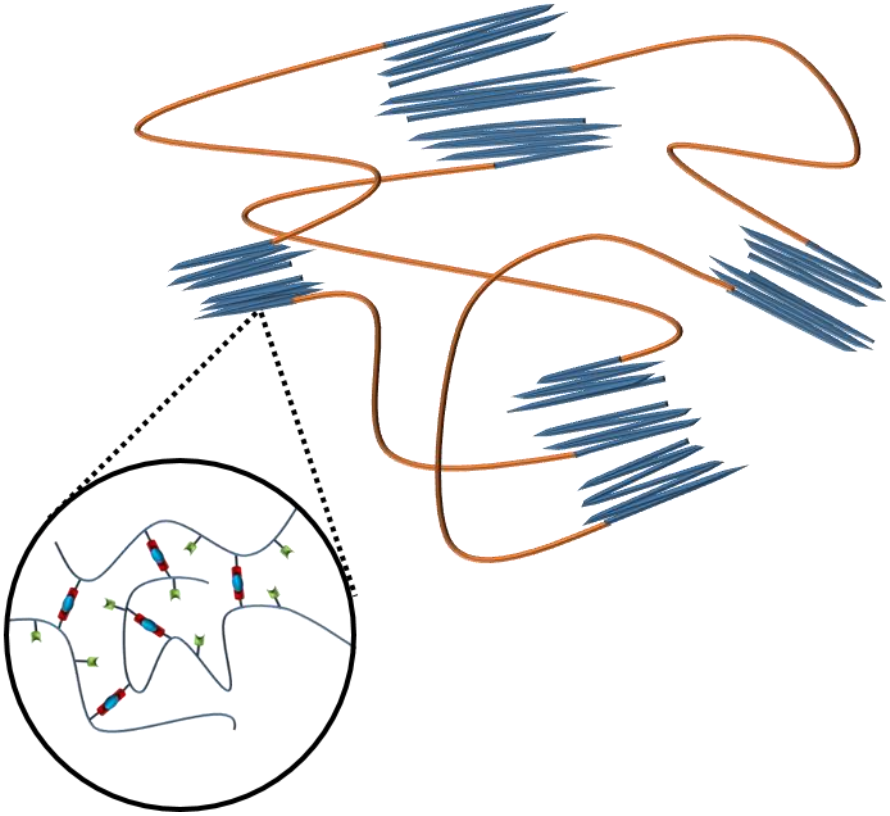
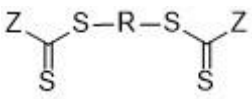
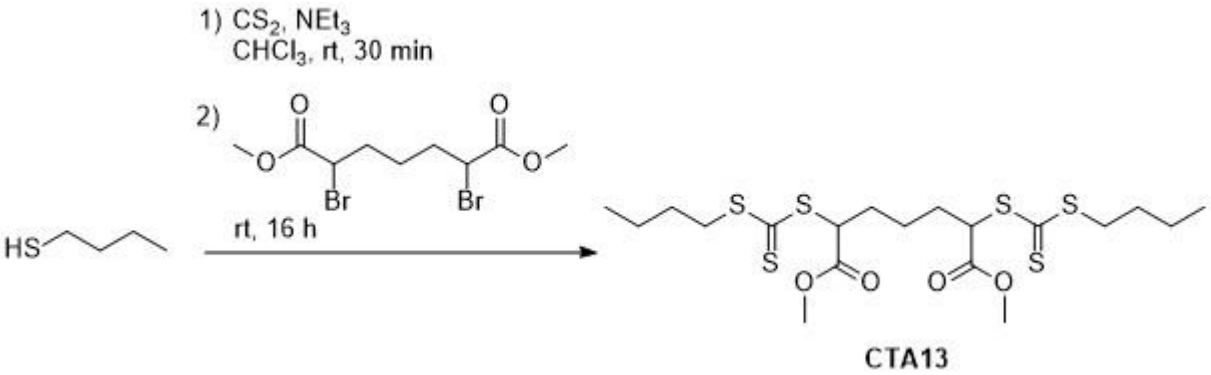


Figure 3.2: Concept of the novel thermoplastic elastomer: the hard phases of the block co-polymers form crystalline domaines below their Tg, which serve as physical cross-links. The outer blocks are additionally connected by dynamic covalent cross-links.



Scheme 3.1: General form of the bifunctional RAFT agent used in the formation of a well defined A-B-A triblock co-polymer.

Therfore, dimethyl 2,6-bis(((butylthio)carbonothioyl)thio)heptanedioate (**CTA13**) was synthesized like displayed in Scheme 3.2.



Scheme 3.2: Reaction to obtain **CTA13**.

The polymerization was conducted with **CTA13** like shown in Scheme 3.3. The focus now is to evaluate the best reaction conditions to get a well-tailored polymer.

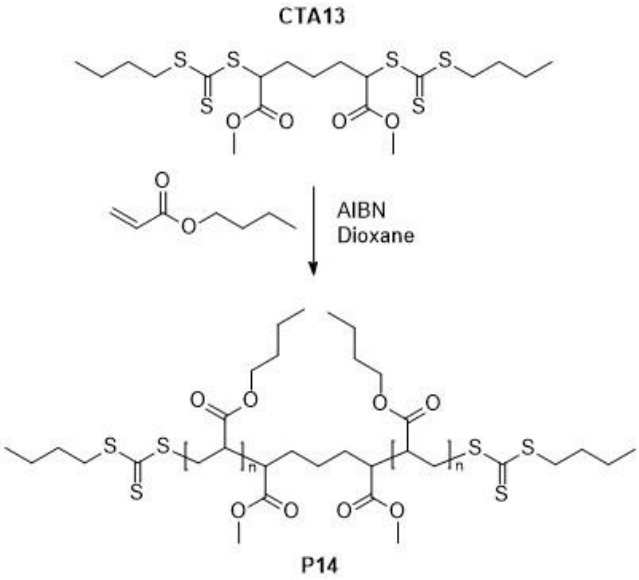
For the outer hard block a boronic-ester exchange system is envisaged. Therefore, a functional monomer has to be synthesized. As a backbone methyl methacrylate (MMA) is suited, therefore a literature procedure3 was adapted to synthesize a MMA based monomer with a diol functionality. The reaction pathway can be seen in Scheme 3.4.

Outlook

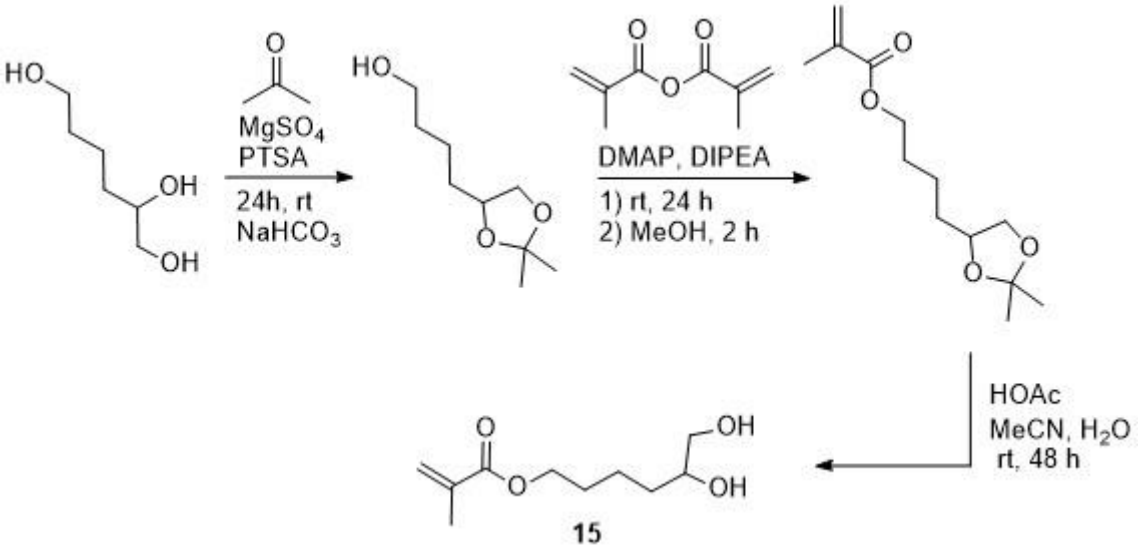
With the building blocks already synthesized, the route of synthesis for the A-B-A triblock is envisaged like shown in Scheme 3.5. First, the soft block composed of nBA is synthesized.

It should have a DPn of around 1000 and have a very narrow Đ to precisely control the properties of the copolymer. The terminal RAFT groups allow the polymer to be extended. Since a direct extension with only MMA is not possible due to reactivity reasons, the outer hard block has to be copolymerized with styrene. MMA and styrene copolymerize almost statistically, so the diol-functional can be built in uniformly distributed.

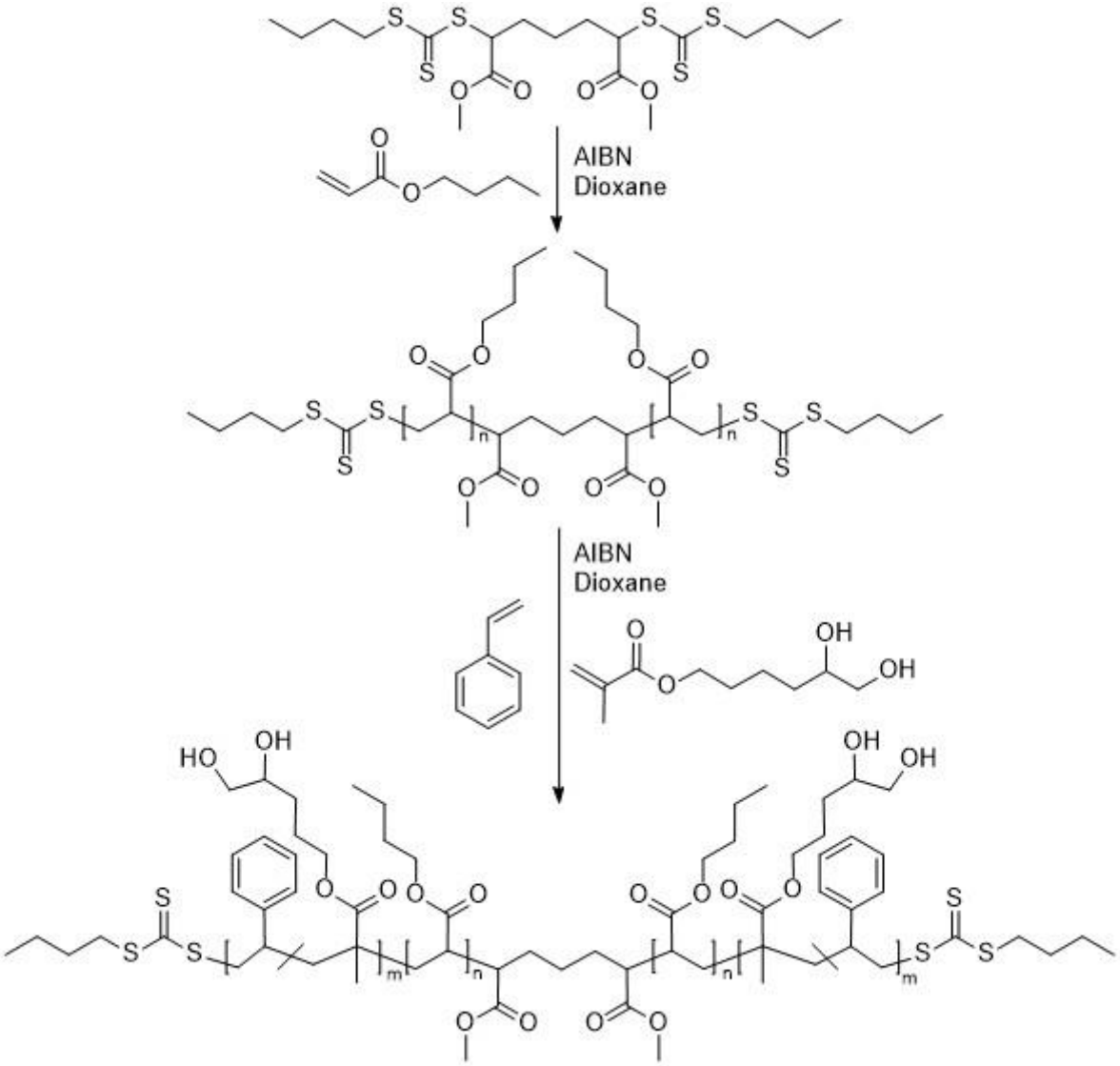
After the RAFT group is removed the polymer will be protected with PBA like shown in Scheme 3.6. This polymer including the cross-linking agent **9** will be sent to the University of Mainz to conduct scattering experiments.



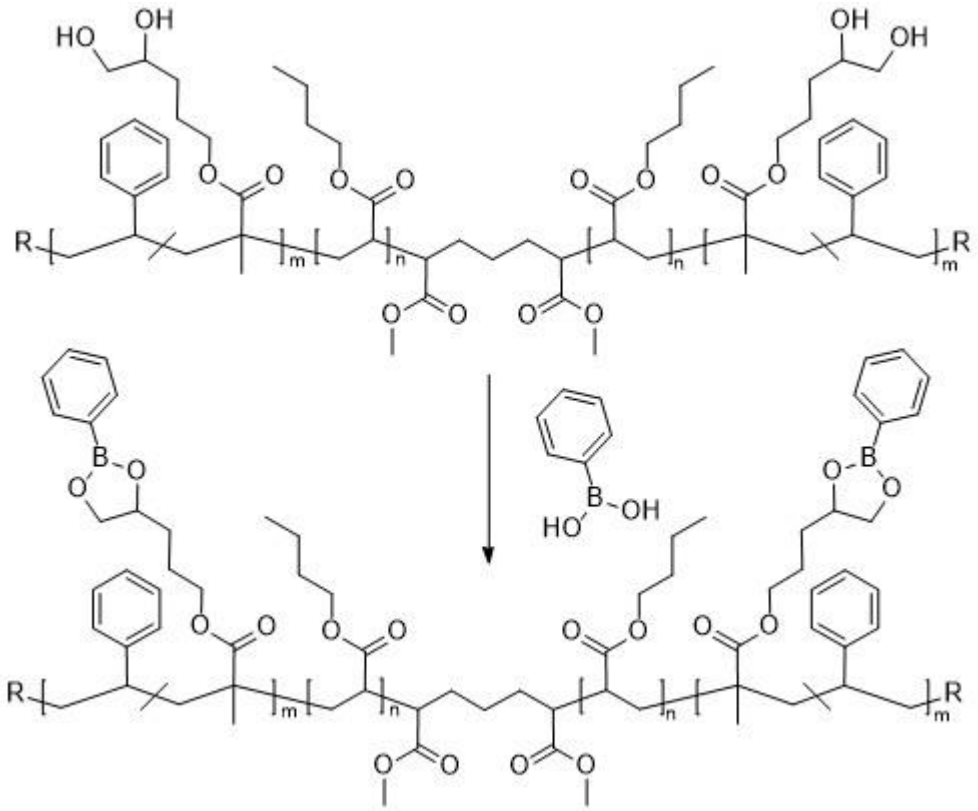
Scheme 3.3: Homopolymerization of nBA with **CTA13** to yield **P14**, representing the inner soft block of the target copolymer.



Scheme 3.4: Synthesis of diol-functionalized monomer **15**.



Scheme 3.5: Synthesis of the A-B-A triblock copolymer.



Scheme 3.6: Protecting the A-B-A triblock copolymer with a boronic ester group.

Methods

The organic syntheses and polymerizations were conducted via standard laboratory procedures.

For air or moisture susceptible reactions, Schlenk techniques were employed.

Purification was conducted via washing/extraction, fractionated distillation and/or column chromatography. Polymers were precipitated in cold solvents to free them from small molecule side products. For the analysis of the small molecules as well as for the polymers 1H NMR and 13C NMR spectroscopy measurements were performed. The polymers were also analyzed via size exclusion chromatography (SEC). The RAFT end group removal reactions were followed via ultraviolet (UV)-visible (Vis) spectroscopy.

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ESR 4 Stefania Traettino

Institution: ESPCI Paris
Supervisor: Michel Cloitre
Period covered: 03/09/2018 to 30/04/2019

Objective of research

Microgels are soft colloidal particles consisting of a crosslink polymer network swollen with water.

Jammed suspensions of microgels interacting through purely repulsive interactions have attracted a lot of attention but quite few studies have investigated the situations where the particles develop attractive interactions. On the other hand, reversible covalent chemistry is now emerging as an interesting strategy for engineering functional dynamic networks with tuneable and stimuli-responsive properties. The objective of this thesis is to design, synthesize and characterize supramolecular networks based on microgel particles used as building blocks, with interact through reversible covalent interactions.

We started from well-defined polyelectrolyte microgels synthesized by emulsion polymerization techniques (made by COATEX).

We studied their rheological properties to better understand their behaviour. This step is still ongoing.

The microgels will then be functionalized by grafting reactive groups capable of forming reversible covalent interactions with neighbours at contact. A possible reaction will be the boronic acid-diol reaction which is known to form boronate esters by condensations, typically above the close-packing concentrations, we will obtain double-networks consisting of permanently crosslinked domains that are connected through tunable reversible bonds.

We will study the microscopic and macroscopic dynamics of concentrated double-networks in relation with the strength of the reversible covalent bonds.

The existence of reversible covalent bonds is expected to be at the origin of novel structural and dynamical properties making these new systems attractive for applications.

The methodology used

Linear viscoelastic properties of different polyelectrolyte microgels and their flow properties were investigated using **rheological technique**.

We used a stress-imposed rheometer and we used two different geometries:

- Cone-plate (d=50 mm, cone angle 2°);
- Couette cell (d=28.7 mm, gap=0.099 mm), to reach higher shear rate;

Oscillatory rheology at small amplitude (SAOS) was performed to test the structure at rest and the morphology of the material when small deformations are applied.

Oscillatory rheology at large amplitude (LAOS) was performed to study the flow behaviour, the yield strain and the yield stress.

Dynamic Light Scattering was used to elucidate the microscopic dynamics of the microgels.

Achivements

We analysed two kinds of polyelectrolyte microgels at different concentrations:

- Repulsive microgels;
- Associative microgels (hydrophobically modified);

They are going to be the building blocks of the double-network.

We investigated the linear viscoelastic properties and the flow properties of both microgels mentioned above.

In particular, we studied linear and non-linear rheology (frequency sweep, amplitude sweep, flow curve etc…) and we paid special attention to the existence of flow instabilities, start-up flow, long-time evolution and aging.

ESR 5 Christina Pyromali

Institution: FORTH

Supervisors: Prof Dimitris Vlassopoulos & Prof George Petekidis

Period covered: 01/04/2018 – 30/04/2019

The objective of this report is to provide an update on the research project progress. Recently, the research interest is focused on providing an extended experimental study of the linear and nonlinear shear viscoelastic properties of metallo-supramolecular transient polymeric assemblies under large shear deformation. This should be done, in order to examine the structure and dynamics as well as the presence of internal stresses after cessation of simple shear flow in the front runner building block in Double Dynamic Networks (DDNs). Thus, the motivation of the current project derives from the inextricable linked relationship between the structures the properties and the function of materials.

These transient networks are based on reversible, relatively weak and non-covalent interactions obtained by metal ligand coordination. The reversibility of the network provides unique properties such as tunability, self-healing, and shape memory features. Moreover, the metal-containing polymeric system may give access to additional magnetic, optical and electro chromic properties that can be helpful for numerous applications such as light

induced adhesives, self-healing coatings and stretchable electronics applications. Last but not least, the possible industrial exploitation of transient networks is based on their processability and rheological behavior under large shear deformation.

The followed research methodology derives the above mentioned objectives and motivation of the research. More specifically, the structure and dynamics of the model networks is investigating experimentally performing linear and nonlinear rheological experiments. The data are collected and analyzed in order to obtain fruitful information on how altering the temperature, the stoichiometric amount or the nature of metal ions, could be manipulated for designing single and double responsive networks with desired properties.

The networks consists of a four-arm telechelic star (star poly (n-butyl acrylate)s functionalized with a terpyridine ligand) and is associated with different metal ions (Zinc Chloride, Copper Chloride, Cobalt Chloride) at different stoichiometric amounts.

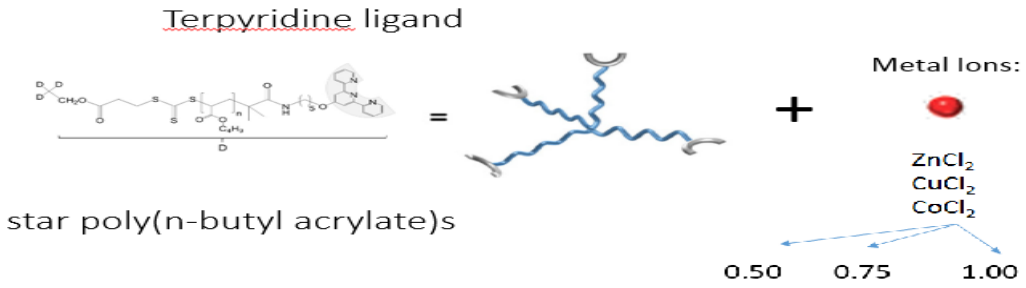


Figure 1: Model system of a four-arm telechelic star associated with different metal ions.

The preliminary results from the experimental study of the model system indicates that the addition of metal ions over the theoretical stoichiometric amount results more stable and higher cross linked network with significantly extended rubbery plateau and shifted terminal relaxation times to lower frequencies. It is also shown that the influence of metal ions in the properties is less prominent at higher temperature [Figure 2].

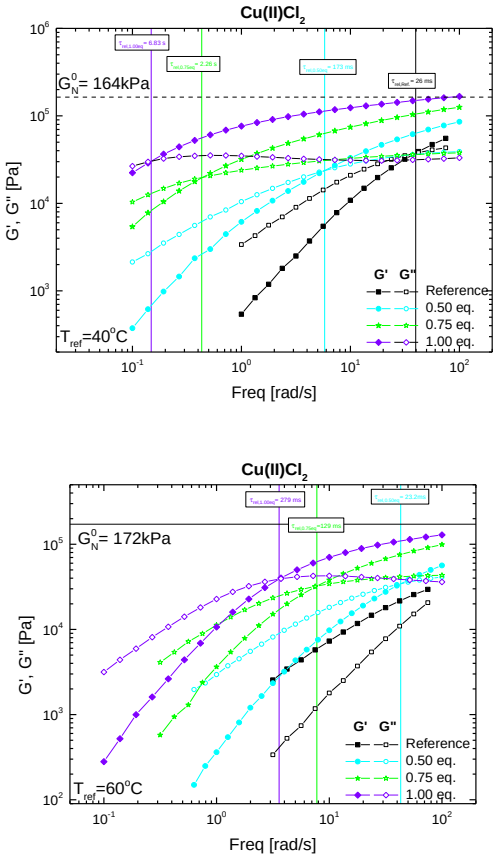


Figure 2: Linear rheology curves of Star250k PnBA with different amounts of Copper (II) ions at 40°C and 60°C.

In addition, strong deviation, beyond the experimental margin error, in the Cox –Merz rule has been observed for most of the samples with added metal ions. This indicates the thermo-rheological complexity of the transient networks caused by the influence of temperature in the disentanglement process, the dissociation mechanism of the metal-ligand complexions and the proportion of dangling chains in the network. The most significant deviation in Cox-Merz rule is observed when Cobalt is added confirming the hypothesis that the higher the binding constants of the metal ions the more promoted crosslinking is achieved [Figure 3].

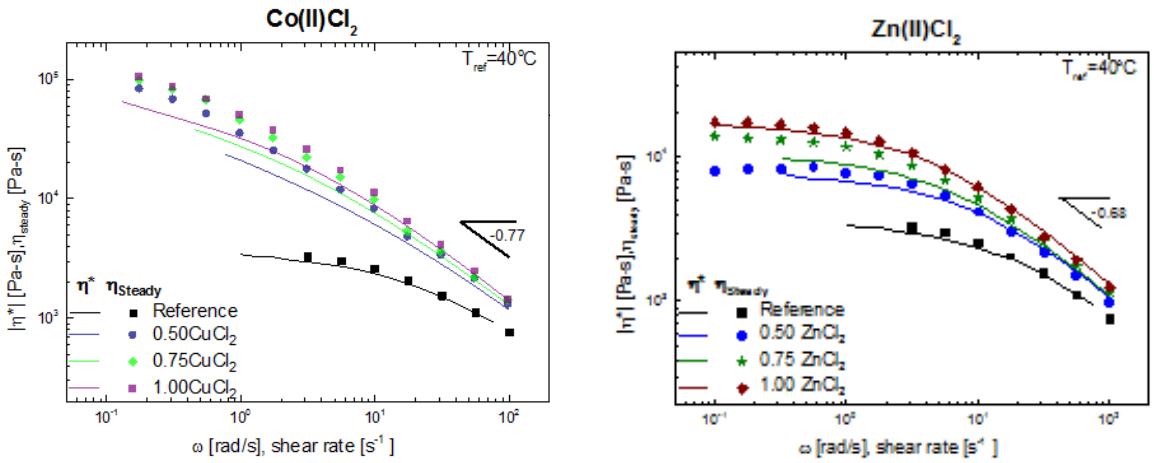


Figure 3: Cox- Merz rule for four-arm telechelic star with different amounts of Cobalt and Zinc at 40°C.

ESR 6 Wendi Wang

Viscoelastic response of double dynamics polymer networks under transient elongation

Institution : DTU

Supervisor : Qian Huang, Ole Hassager

Period covered: 01/06/2018 – 30/04/2019

Objectives of research

As part of the DoDyNet project, the objective of this PhD project is to understand the exact role of molecular parameters such as entanglements, dangling ends and chain architectures on the dynamics of Double Dynamics Networks (DDNs). The project will focus on studying the nonlinear extensional rheology of different DDNs. In order to relate the rheological results to mechanical properties towards applications, the fracture behavior of DDNs in tensile mode will also be investigated.

To begin with, rheological and mechanical properties of polystyrene with hydrogen bonding have been investigated. Recent research work shows that at room temperature, brittle polystyrene can become flexible by stretching polystyrene melts at a rate faster than the inverse rouse time, followed by rapid quenching below Tg. The long-lasting flexibility and good humidity resistance make polystyrene suitable for optical fibers. However, improvements are required to prevent potential cracks while bending. This project investigates if such improvement can be achieved by introducing hydrogen bonding. The rheological and mechanical properties of polystyrene with different pendant acid group proportions, which can form hydrogen bonding, are studied and compared to pure polystyrene sample.

Methodology

Three different PS based materials (pure polystyrene, Tg = 100°C; polystyrene containing 5% acid group on the polymer chains, Tg = 114°C; polystyrene containing 9% acid group on the polymer chains, Tg = 122°C) are characterized by the following techniques:

- Small amplitude oscillatory shear
- Uniaxial extension
- Tensile test
- Three-point bending test

Achievements

- The LVE properties indicate a similar number of entanglements per chain for all the samples, meaning that the acid groups do not form hydrogen bonding at high temperature above Tg.
- Different samples show similar extensional behavior at high temperature above Tg.
- The formation of hydrogen bonding at room temperature has been confirmed by IR-ATR spectrum.
- According to tensile tests at room temperature, the presence of hydrogen bonding can increase yield stress of flexible PS.
- According to three point bending test at room temperature, the presence of hydrogen bonding helps enhancing ductility of PS based material.
- Step strain measurement shows that by increasing hydrogen bonding content, the reversibility of the material is improved.
- Preliminary experiments on PS ionomer (with ionic interactions) have been carried out, sample stability and bonding force need to be improved.

To sum up, from experimental results, we have seen while hydrogen bonding do not influence linear and nonlinear properties for selected PS based samples at melt state. In the solid state, they enhances yield stress and also help improving ductility and reversibility of the polystyrene.

ESR 7 Carole-Ann Charles

Institution : Université de Montpellier

Supervisors : Christian Ligoure, Laurence Ramos

Period covered : 15/01/2018 – 30/04/2019

Objectives

- Study of the double dynamic networks behavior as a function of the lifetime and elastic modulus of the networks constituting the latter.
- Understand and rationalize the impact of the double dynamic on the elasto-capillary effect in said networks.

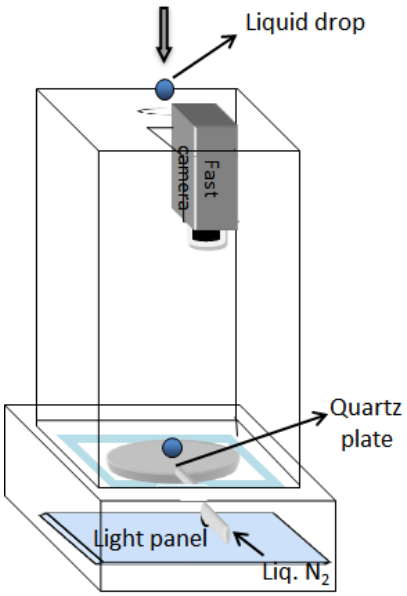
- Relate these effects to the nonlinear response in shear or other flows of the double dynamic networks and to the adhesive properties.

Methodology

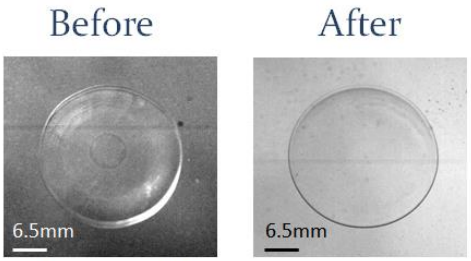
- Drop impact using the inverse of Leidenfrost effect

Achievements

I have been working on improving and characterizing a setup allowing the study of drop impact dynamic with minimized shear dissipation. This setup uses the inverse of Leidenfrost effect by performing the impact on a thin layer of liquid nitrogen that evaporates when the drop at ambient temperature comes into contact with it, forming a vapor cushion on which the drop can expand radially freed from shear dissipation.

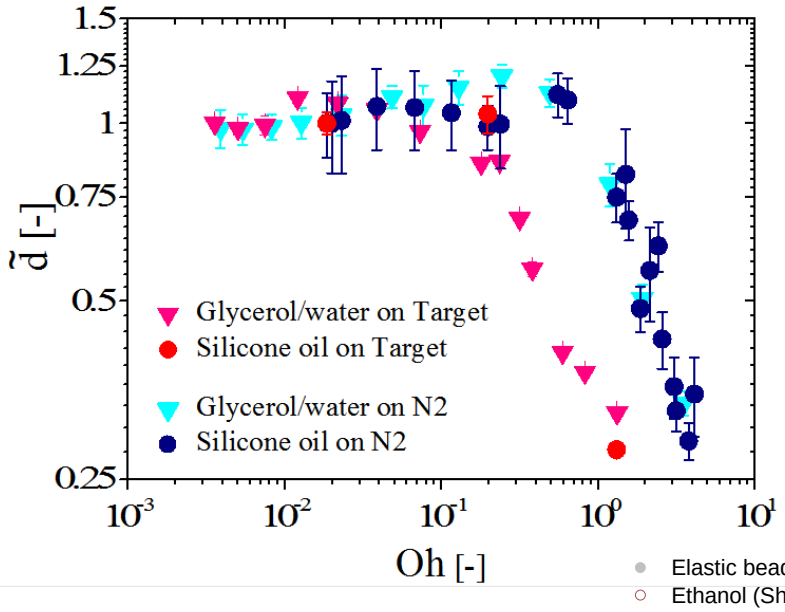


By changing the surface of impact from a silicon wafer to a quartz plate, a semi-automatic analysis of the data is now possible and a study of the sheet thickness field is conceivable thanks to the better contrast.

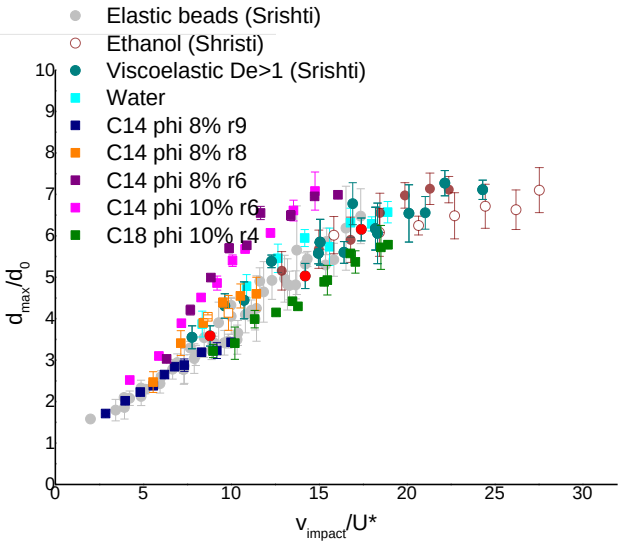


S. Arora et al., 2017

Subsequently this setup will be used to study the impact of transient networks including double dynamic networks and will allow to rationalize the different roles of inertia, elasticity, capillarity and dissipation.



As a first step, the setup was tested with Newtonian fluids of different viscosities. The maximum expansion of the sheet of silicone oil on liquid nitrogen compared to the maximum expansion on a target of size similar to the one of the drop shows that the shear dissipation has been successfully reduced.



The next step was to use this setup with microemulsions reversibly linked by telechelic polymers with different modulus and relaxation times. These microemulsions were impacted from several heights to highlight the effect of the impact velocity on the dynamic of the impact. These microemulsions have a characteristic relaxation time and its effect was also rationalized.

In parallel, the study of the sheet thickness field is being done for mixtures of glycerol and water colored by water soluble nigrosine and analyzed using Beer-Lambert law.

ESR 8 Consiglia Carillo

Institution : FORTH

Supervisor : Dimitris Vlassopoulos

Period covered : 01/09/2018 – 29/04/2019

The aim of my project is to study the dynamics and nonlinear shear response of reversible covalent systems and double networks systems with the ultimate goal to tailor rheological properties of networks via interplay of bond and segment dynamics. The investigation involves the combination of distinct properties of two classes of networks and crosslinks, to impart large mechanical strength, deformability, swelling and self-healing, in order to obtain materials suitable for different applications.

Rheological and mechanical properties will be linked to the fracture mechanisms and to the elongational properties, in order to establish the connection between network structures, chain mobility and physical properties.

Linear and nonlinear rheological tests are performed in order to investigate the macroscopic properties of the samples such as stability, relaxation time spectrum and shear thinning or thickening behavior, which are connected to its microstructure.

In this period, two systems are being investigated, one model provided by Université catholique de Louvain and one industrial supplied by TESA.

The former system is an ABA triblock (*Fig.1*) which has to be combined with a second network characterized by a short lifetime in order to obtain a double network. The triblock is made of two external block of polystyrene and one central soft block of poly-n-butyl acrylate (PS-PnBA). The effects of the length of polystyrene chains were studied using two different samples (PS(13K)-PnBA and PS(6.3K)-PnBA).

Figure1. Scheme of the studied copolymer.

The relaxation spectrum of the sample, reported in *Fig.2*, was investigated over a wide range of frequencies. The sample with longer polystyrene chains exhibits slightly slower dynamics. In particular, the low-frequency scaling of the storage modulus as $G' \sim \omega^2$ implies the absence of phase separation at the particular temperature range.

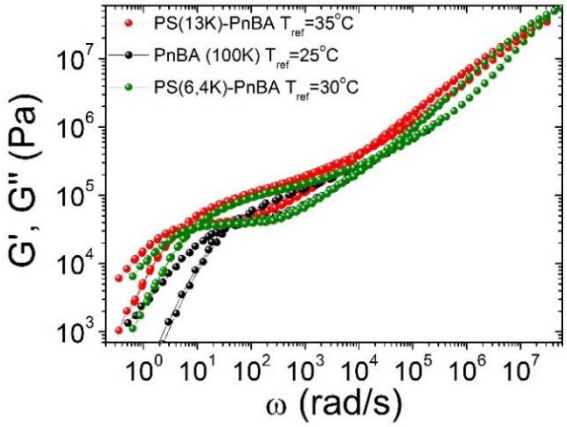


Figure2. Linear viscoelastic spectra for PS-PnBA copolymers and for PnBA are reported on the right

The latter system is an industrial dual crosslinked network. As showed in *Fig.3*, it is made by one single network with two types of crosslinks, permanent and transient.

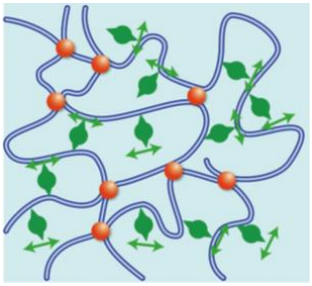


Figure3. Single network with dual crosslinks.

Its rheological behavior is compared with the behavior of the single component (polymer without crosslinks) and with the systems with only physical crosslink and with only chemical crosslinks. In this way, it is possible to investigate the effect of the crosslinks on the system in order to be able to modify and, hopefully, improve its properties. As can be seen from Fig.4, at low temperatures the samples with only physical (ionic), only chemical (covalent) or with both crosslink (double) exhibit very similar behavior, contrary to what happens at high temperatures.

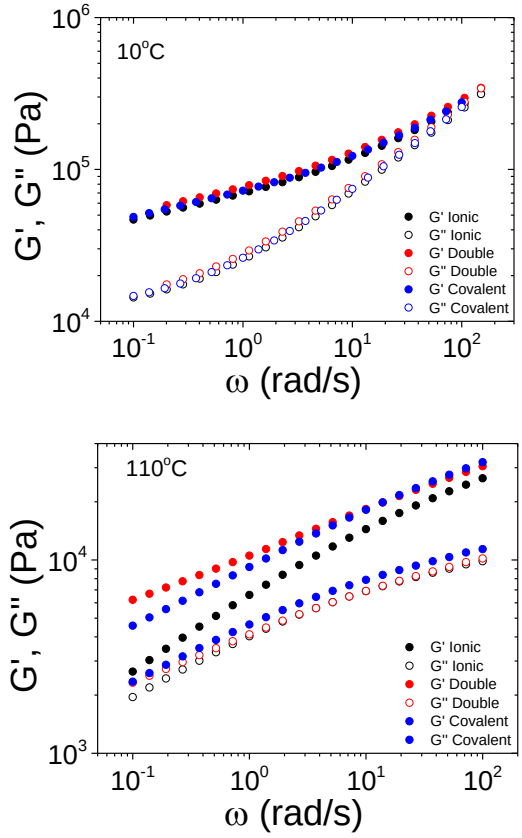


Figure4. Frequency-dependent G' and G'' measured at 10℃ and 110℃.

ESR 9 Simone Sbrescia

Institution : DSM / UCL

Supervisor : Michelle Seitz, Evelyne van Ruymbeke

Period covered : 01/05/2018 – 29/04/2019

Objectives of research

Understanding the unexpected and undesired high temperature mechanical behavior and failure mechanism of soft DD-TPEs, with the aim to build a global physical picture on the origin of sample breaking as well as the entire behavior during deformation. Based on this understanding, we will explore to what extent adding additional dynamics (e.g. combination of types of physical crosslinks, covalent bonds, or via crystal morphology) can improve these key mechanical properties.

Methodology

Investigating, by tuning composition and molecular weight, the high temperature linear and non-linear mechanical properties via mechanical tests (i.e. tensile tests, DMTA, fracture tests, etc.) and the morphology in both the deformed and undeformed state (AFM, in-situ X-ray). The picture that we aim to build up, that explains the deformation behavior of this class of materials, will be supported by the results achieved from the mechanical tests and from statistical tools and models that we will develop, able to capture and predict key parameters of the material's microstructure and mechanics.

Achievement

So far, we screened the linear and non-linear properties of these materials by tuning their composition and molecular weight. We identified several zones of deformation in which composition and molecular weight act differently, with different dynamics, in improving materials properties. With the use of a statistical tool and based on the results we obtained we are building-up a picture which is able to explain the result obtained and that will guide us to the future steps necessary to move forward in understanding the high temperature mechanical behavior of soft DD-TPEs.

ESR 10 Paola Nicolella

Institution : Johannes Gutenberg-University Mainz
Supervisor : Sebastian Seiffert
Period covered : 07/09/2018 – 29/04/2019

Objectives of research

The main objective of my research is to characterize the structure of double dynamic networks by the means of light scattering techniques. In order to achieve this goal, it is necessary to characterize first the single components of a network, then a single dynamic network and then finally the double dynamic network.

Another objective of my research is to investigate the diffusion in double dynamic networks by the means of probe diffusion techniques.

The combination of light scattering and probe diffusion techniques, allows to investigate the samples in the whole spectrum, from the nano- to the macro- scale.

Methodology used

The most used technique used in this research is light scattering, both static and dynamic.

A complementary technique will be fluorescence correlation spectroscopy.

Achievement so far

Functionalization of 4-arm Poly-ethylene-glycol with terpyridine and its characterization with light scattering.

Synthesis of 4-arm Poly-ethylene-glycol functionalized with terpyridine and with an additional functional group where another polymer will be attached, in order to achieve the double dynamicity.

Development of a tutorial review on scattering and probe diffusion techniques.

ESR 11 Hongwei Liu

Institution : UNaples

Supervisor : Giovanni Ianniruberto

Period covered : 01/09/2018 – 29/04/2019

Objectives of **research**

We are aiming at simulating the rheological behavior of polymer networks (hybrid double networks) using multi-scale methods. Such hybrid double networks have two kinds of stickers, one is reversible and the other one is somewhat permanent.

The methodology used

To simulate the movement of molecules, we resort to Browninan dynamics simulations. Besides, periodic boundary conditions are applied to simulate a huge number of molecules but only using several thousands of molecules.

Achievements so far

Up to now, we have finished the development of the program for the 2-D transient networks with multiple stickers. By plotting the conformations of the molecules, we can check if the program runs as we wish. After correcting and improving the program, we compared the simulation results with some analytical solutions so that we can say that our program is reasonable. In the future, we will continue to expand the 2-D program into a 3-D and with two kinds of stickers one.

ESR 12 Yanzhao Li

Institution : UCL

Supervisor : Evelyne van Ruymbeke

Period covered : 01/09/2018 – 29/04/2019

Objectives of the research

In the DoDynet project, my objective is to investigate and modelling the linear dynamics of DDNs, so as to deepen and broaden the molecular understanding of the soft materials, which will benefit designing of novel materials for application. Their main characteristics (composition and architecture of the building blocks, degree of interpenetration, type of interactions between the sub-networks, and lifetime of the interactions, etc) will be systematically varied to understand their influence on DDNs structure and dynamics. I will

also attempt at modeling local diffusive process of DDNs. In order to model their viscoelastic behavior, before the work of DDNs, I will start from the tube model developed at UCL to predict the properties of supramolecular entangled polymers. My main contribution will be to extend it to an entangled polymer network governed by two different supramolecular dynamics. Specific sets of samples will be measured, which will help understanding the influence of their composition parameters, and the statistical composition will be determined. I also will work on developing a model to determine the rheology of entangled sticky chains, and including the sticker dynamics in modelling and determining a strategy to describe experimental data.

The methodology

The experimental techniques are mainly based on rheological tests, which is performed on Strain-controlled Rheometer or stress-controlled Rheometer as well as filament stretching rhoemeter. The modelling part is based on the Tube model, as shown below with the TMA (time marching algorithm) methods.

Achievements

So far, I am focused on understanding the dynamics of telechelic star polymer(single polymer network) which combines two metal-lingand cross links with distinct relaxation mode, as shown in figure(1) and (2) below. Reversible polymer network based on telechelic PnBA star polymers, the molecular mass is 250kg/mol and entanglement molar mass is 18kg/mol. The metal ions that is used to create metal-ligand complex are zinc, copper, cobalt and nickle.

(1) telechelic star polymer with two metal-ligand crosslinks (2) Distinct relaxation of telechelic star polymer with different metal ions

A. Rhelogical test

Firstly, Zn2+ and Cu2+ were blended in the telechelic star polymer, take the 60℃ for an example, the results are shown in the figure(3), the stoichiometric amount of metal ions are varied, from 0.5eq. (ideal amount to form network) to 1eq. (excess state). Based on the rheological test, the blend shows a relaxation behavior between the single metal ions, and close to Zn2+. The blend shift to the middle with the increase of amount of the metal ions.

(3) rheologist test on different stoichiometric amount of metal ions of Zn2+ and Cu2+ blend in telechelic star polymer at 60℃

And when the amount of metal ion increase to 2.5eq., some interesting relaxation behavior appears, as shown in Figure (4), the blend shows a slower relaxation than both the single metal ions. And also 2.5eq. Zn2+ shows a slower than 2.5eq. Cu2+, in contrast with the lower amount of metal ions, such as 0.5eq., 0.75eq., and 1eq.. The same relaxation behavior is also observed on the blend of 0.5Zn2+ (0.75eq.) and 0.5Co2+(0.75eq.). The explanation for this interesting relaxation behavior can be considered as the transformation from mono-complex to the bis-complex. But it should be found an method to detect and further demonstrate it.

(4) Rheological test measured at 100℃(left) and 80℃(right) based on 2.5eq. Zn2+ and Cu2+ blended in telechelic star polymer

B. Modelling part

The modelling part of the experimental result based on the Tube model with the TMA methods proposed at UCL, Two parameters are defined, proportion of the dangling ends and the proportion of the time during which a ticker is free, to realize the modelling process. Take 0.5eq. Zn2+ and 0.5eq Cu2+ as an example, as shown below.

C. Some questions

1. The molecular pictures should be proposed to explain the relaxation behavior of the different material systems?

2. The other detecting techniques, such as NMR, UV, etc, should be used to confirm the transformation of the mono-complex to bis-complex?

3. Understanding the relationship between the modelling result and the distinct relaxation behavior?

ESR 13 Jianzhu Ju

Application property of double dynamics polymer networks

Institution : ESPCI

Supervisor : Costantino Creton

Period covered : 01/09/2018 – 29/04/2019

My project (ESR13) will be related to application property of double dynamics polymer networks. The main task will be combining property measurement and mesoscopic dynamics/structure characterization. To achieve the goal, diffusing wave spectroscopy (DWS) is applied to measure the dynamics in polymer network during fracture and other different condition.

DWS is sensitive to mesoscopic dynamics of polymer network and compatible with other characterization methods. Combined with macroscopic mechanical measurement and mechanophore study on bonds breakage, we will be able to provide a hierarchical fracture model and even predict fracture precursor long time before macroscopic fracture.

In the current stage, I mainly working on devices development, including mechanical part (tensile machine, force measurement and motion control) and optical part (optical alignment and image acquisition/processing). For mechanical part, a bidirectional extensional stage has been designed and fabricated, as shown in Fig. 1. With a custom bidirectional screw shaft, the center of the sample will stay constant during extension, which provides an ideal condition for in-situ optical testing. The set-up will be ready in June, when the combination with DWS and other testing methods will be tested.

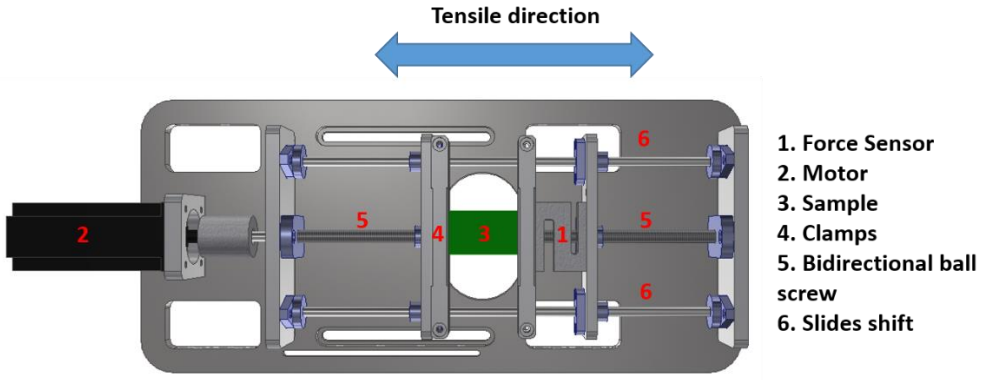


Fig. 1 Bidirectional extensional for DWS.

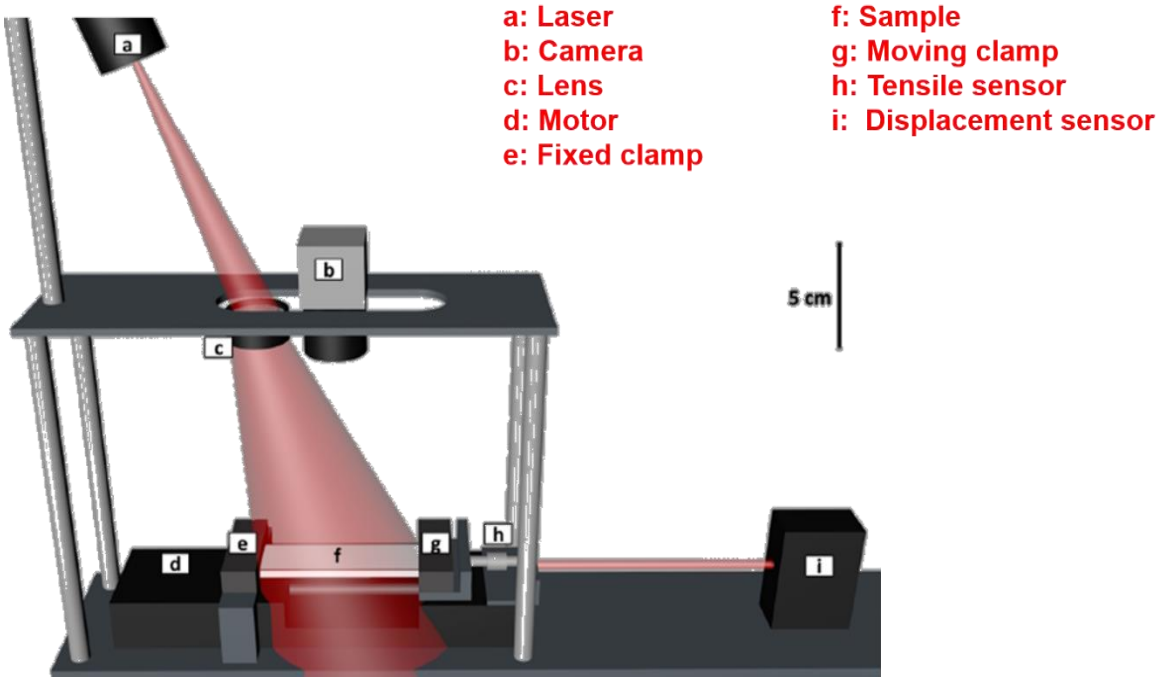


Fig. 2 Experimental set-up of DWS tesing.

In the meantime, preliminary experiments have been performed in Montpellier University with Prof. Luca Cipelletti. We prepared PDMS elastomer with the addition of TiO2 nanoparticles (d=258 nm, 0.25 wt%). The experimental set-up is shown in Fig. 2. Multi-step delayed fracture testing was applied on the sample under characterization by DWS. Displacement and stress results are measured by displacement and force sensor, respectively, as shown in Fig. 3(a). Correlation as function of time after each loading can be calculated from multy-speckel DWS testing, follow the equation:

$$C_I(t,\tau) = \frac{\langle I_P(t) I_P(t+\tau)\rangle_P}{\langle I_P(t)\rangle_P \langle I_P(t+\tau)\rangle_P} - 1$$

Where $I_P(t)$ and $I_P(t+\tau)$ are intensity of pixel of interests at t and $t+\tau$, respectively. After ensemble averaging over pixels, correlation can be calculated and it can be expressed as:

$$C_I(t_1,\tau) = Aexp\left(-\left(\frac{\tau}{\tau_0}\right)^P\right) + B$$

So that we can investigate the dynamics as a function of t, indicated by decorrelation time τ_0. τ_0 results are shown in Fig. 3(b). From 1st to 5th step, it can be discovered τ_0 increases with time and reach plateau at later stage, with similar increase rate. The increase of τ_0 corresponds to the stabilization of the system and force relaxation. However, in 6th step, even macroscopic fracture happens after 2400 s, τ_0 value is much lower than the previous steps right after loading. Around 800 s after 6th loading, τ_0 begins to decrease, indicating the acceleration of the probe particles movement. From the results, we can conclude that during 6th steps, fracture precursor can be observed by DWS, and the time scale of τ_0 can be related to mesoscopic change in the polymer network.

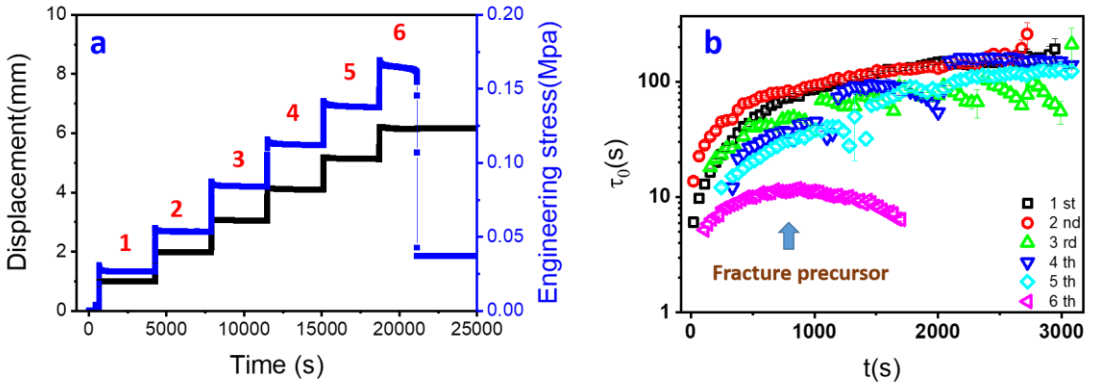


Fig. 3(a) Displacement and stress results during multi-step extension. During 6th step, 2400 s after the loading, macroscopic fracture can be discovered on force results. (b) τ_0 as functions of time after each loading.

Based on the results, the application of DWS has been tested with PDMS as a model material and fracture precursor has been successfully observed. With the development of mechanical parts and optical parts, mesoscopic behavior in different network system will be further investigated in the future.

Samples

Samples have started circulating between members of the network. Two triblocs ABA (used in 1A and 1D systems) were sent from UCL to FORTH. tesa has also sent specific samples for the ESRs in FORTH to work on. Carole-Ann Charles from Université de Montepellier has been working on the samples of her university which are connected microemulsions.

Training

Our training strategy is aimed at providing the ESRs with a unique background in the industrially important and scientifically challenging inter-disciplinary field of synthesis, physical chemistry and macroscopic properties of polymer networks and gels, as well as in transferable and specialized skills that are the key for success in academia and industry. As explained below, exposure to both academic and industrial environments will offer our ESRs the opportunity to develop competitive professional profiles and acquire a high degree of expertise on how to tackle problems across disciplines with a synergetic approach. This will make them highly valuable for the EU industry in wide-ranging fields encompassing cosmetics, daycare, coatings, foodstuff and pharmaceuticals.

The training programme is divided into several tasks, both at the local and at the network level. In all training activities, emphasis will be given on combining courses with practical work. To effectively implement the training program, we have designated a **Training Officer** (G. Iannirubertо, UN), who will oversee and report annually on the training progress. To ensure successful training and scientific development of the ESRS, they will have to define a **Personal Career Development Plan** (PCDP) in consultation with their supervisors. This dual structure will ensure that DoDyNet follows the European Charter of Researchers in employing/training ESRs.

In the Personal career development plan (PCDP), each ESR together with his/her research advisors shall establish a PCDP, which shall provide the pathway to evolve as a researcher, undertake initiatives nurturing entrepreneurship and creativity, and develop a professional spirit. Central to the PCDP is a clearly defined research project. The inter-disciplinarity of the project will be ensured through a joint supervision by senior scientists from different groups. The PCDP was filled in by each ESR individually in the month following their enrolment in DoDyNet.

Local Training: the main element of local training is the individual PhD project of the ESR

Besides this, ESRs will have the opportunity to take local advanced courses choosing from the whole panel of specialized courses available at their home institution or secondary institution (the detailed lists are available on the websites of the Institutions), and credited with ECTS units. Complementary skill-related courses, delivered in each partner's home institution, will also be offered at the local level to the ESRs. They are designed as 1-day short courses and provide knowledge in the field of communication/dissemination of research work:

Proposed list of transferable skills at the local level

BASIC TRANSFERABLE SKILLS	ADVANCED/SPECIALIZED SKILLS
Presentation skills	Knowledge management
Safety in work environment	Communication and media training
Introduction to research methodologies	Communication

English for non-native scientists (full semester)	Paper / proposal writing
Local language for non-native scientists (full semester)	Technical presentations (oral, poster)
IT courses (MS-office, SAP, Maple, programming)	Intellectual property (IP) rights

Regarding the Network-wide event: they are designed to provide ESRs with transferable skills as well as a broad basic background in scientific areas of relevance to DoDyNet, in order to give ESRs the opportunity to widen their grasp of the field and enhance their knowledge, access complementary skills and interact with the other participants for putting their project into broader perspective. These events will include elementary and advanced modules, two industrial workshops, a summer school and project meetings.

For this period, the students have already followed: Elementary Modules (September 2018, FORTH, Crete), Industrial Workshop (January 2019, DSM, The Netherlands) and Advanced Modules (January 2019, DSM, The Netherlands). Visiting experts from our International Advisory Board were invited at each event. These experts presented a lecture or a course and attended the ESR Presentations during the Project Meeting which allowed them to have interactions and discussions on the ESR's individual work progress, methods, results.

The Elementary modules provide the basics in each sub-field at a level appropriate for all ESRs, since all must broaden their knowledge and establish a common language with other researchers. We chose to change the initial dates when this Elementary Modules were planned (initially late July) so that all the ESR would be recruited and could then participate to the Elementary Modules. Organizing them in September allowed us to organized only one set of Elementary Modules and thus enabled us to organize more Advanced Modules at a later stage as all the ESR were able to follow the Elementary Module at the beginning of the project.

The full programme of the Elementary Modules can be found in the Appendix 1. The invited lecturers for this event were Daniel Read (University of Leeds, UK), Giuseppe Marrucci (University of Naples) and Emanuela Del Gado (Georgetown University, USA).

The Advanced modules provide ESRs with a deeper knowledge in a specific field related to their individual research project. The Advanced Modules and Industrial Workshop took place in January and were organized by DSM in the Netherlands. The full programmes can be found in Appendix 2 and 3. The invited lecturer for this event was Ralph Colby (Penn State University, USA).

All Modules (Elementary and Advanced) and Industrial workshop are followed by an evaluation by ESR. A Training Report follows with the points to highlight and take into account following their feed-back.

The next event organized is a Summer School on “Transient and complex polymer networks” in Capri in July 2019. Here all the members of our Advisory Board will be attending and giving a lecture.

Deliverables

You will find here the table resuming our deliverables and the date when they were issued. The main differences in the dates initially planned at the beginning of the project and the actual time when the deliverables were issued can be seen in two deliverables.

Firstly, for the Minutes of the Kick-off meeting, this was due to a computer problem which made us lose all the notes made during the Kick-off meeting. It made it difficult for us to issue a complete resume of this meeting in due time.

Secondly, as explained above, the Elementary Modules were organized in September 2018 instead of July 2018 to enable all the ESR to be present at the first meeting and following these Elementary Modules. As we knew we were doing good progress in the selection process and that we would be in advance in the recruitment timetable, we thought it made more sense to wait one month for all our ESR to have started on the project and organize the Elementary Modules for all of them in one event.

This also implies that all our next meetings will be slightly delayed due to this strategical decision. Thus, the Advanced Modules I and the first Industrial Workshop will take place at the end of January 2019 instead of late November 2018.

WP1	D1.9	D2	Minutes Kick-off Meeting	UCL	24 May 2018
WP1	D1.21	D102	Minutes of Supervisory Board	UCL	8 February 2018
WP1	D1.20	D100	Consortium Agreement	UCL	20 February 2018
WP 1	D1.1	D3	IPR Protocol	UCL	13 February 2018
WP 9	D9.1	D36	Website	CNRS	8 February 2018
WP 1	D1.2	D5	Recruitment of ESR round 1	UCL	3 May 2018
WP 1	D1.10	D4	Minutes of Supervisory board	UCL	3 May 2018
WP 1	D1.23	D101	Data management plan	UCL	24 April 2018
WP 1	D1.8	D6	Recruitment of ESR round 2	UCL	27 July 2018
WP 7	D7.1	D21	Elementary Module I	UN	9 October 2018
WP 1	D1.4	D9	Recruitment of ESR Final round	UCL	2 October 2018
WP 1	D1.11	D8	Minutes of Supervisory board	UCL	13 November 2018
WP 1	D1.17	D7	Yearly ESR Progress report	UCL	6 November 2018
WP 10	D10.1	D1	EPQ Requirement n°1	UCL	8 November 2018
WP 7	D7.3	D22	Advanced Modules I	UN	7 February 2019
WP 7	D7.9	D23	Training Report	UN	2 January 2019
WP 8	D8.1	D33	Industrial Workshop I	DSM	19 February 2019
WP 1	D1.22	D103	Progress Report *(updated)*	UCL	1 May 2019

Table of Deliverables achieved to date of the Progress Report (up to April 2019)

Milestones

The following Milestones have been submitted so far. The Milestones related to first scientific results have been delayed as the ESR student working on these samples was only recruited in March 2018. This means the Milestones in red in the table below (4 and 6) will be available really shortly.

The Project check was initially planned during our next project meeting in January 2019 (Month 14) but due to an agenda issue, our Project Officer will carry out this Mid-Term Check during the project meeting that will take place in May 2019. The programme, dates and venue of this Mid-Term Check have already been determined. It will take place in DTU, Denmark on the 6th and 7th of May 2019. The full programme can be found in Appendix 4.

Table of Milestones achieved to date

1	Kick-off meeting	UCL	30 Nov 2017
2	Recruitment end	UCL	15 Sept 2018
3	Researcher Declarations on Conformity	UCL	9 Oct 2018
4	Sharing DD thermoplastic elastomers (DD-TPE) and adhesive among the consortium	DSM Ahead	01 Jul 2018
5	Synthesis of systems 1.A. and distribution among the partners	UCL	Nov 2018
6	Synthesis of systems 1.C. and distribution among the partners	UCL	01 Oct 2018
7	Synthesis of the first systems 1.B. and 1.D., and distribution among the partners	UCL	1.D Nov 2018
20	Webpage online, advertised open positions	UCL	19 Dec 2017
22	Planned recruitment completed	UCL	02 Oct 2018
23	All recruited fellows enrolled in PhD programme	UCL	Nov 2018
24	Project check at month 13	UCL	Planned 6 - 7 May 2019

Colour explanation:

In red – Milestones related to samples that will be available shortly.

In orange – Date changed, not the same as initially planned.

3. Recruitment strategy

Here we will detail the selection process of the ESR candidates for the DoDyNet project.

The job offers were drafted by the leading scientists and collected by the coordinator, Evelyne van Ruymbeke. Each Early Stage Researches (ESR) positions were described in detail taking into account the specificities of the research area covered by each PhD candidate, the timing and duration of the positions, their location and their supervisors. A description of the entire DoDyNet project was also included. The full ESR descriptions and vacations can be found as they were published in Appendix 5.

The finalized descriptions of these ESR positions were published on different websites to maximize the visibility of these job opportunities (mainly SoftComp: https://eu-softcomp.net/, Euraxess : https://euraxess.ec.europa.eu/ and European Society of Rheology: https://rheology-esr.org/).

They were published on Euraxess at different time intervals. They were first online on Euraxess on the 22nd of October 2017. The deadline to submit applications was 30th of November 2017.They were then published a second time on the 14th of December 2017. The deadline fixed was the 31st of January 2018.

The third announcement for these positions was done on the 13th of February 2018 and the deadline was the 30th of March 2018.

The last few vacant job positions were then published with a deadline fixed on the 30th of June 2018.

As soon as the website of the project was online in December 2017, the different offers were also published on the following link : https://www.dodynet.eu/.

The vacant positions were also published on several websites, specialized on the topics studied in DoDyNet. Thus, the job offers were published on the SoftComp website (https://eu-softcomp.net/) and the website of the European Society of Rheology (https://rheology-esr.org/).

All the applications were sent to the project manager by mail to the same email address: dodynet-manager@uclouvain.be. The application were then transferred to the different professors in charge of each specific ESR position.

The description of the different job positions were also sent by academics to their own personal contacts by email.

The application were sent individually to the academics concerned by the post so they studied the applications individually for the PhD position that concerned them. They made a pre selection of candidates and then concerted with other academics to take the final decision on the student to take on. Thus we can say that the recruitment procedure followed an individual process but ended in a concerted decision.

When the rules of the University asked for a concerted process then all the recruitment strategy was done jointly. It was the case for Naples were the candidates who had relevant profiles did a joint skype conference with academics of the consortium, the project coordinator Evelyne van Ruymbeke, and the professor from Naples University. So in this case, the selection was done jointly to follow the rules of this university.

The selection procedure to shortlist candidates was quite straightforward as we lacked good applications. In most cases, the PhD student chosen as ESR was the only valuable application for the job position. However, the question was highlighted for 2 positions: in Naples and in

Mainz. For Naples, the procedure of the university implied a concerted action in the selection procedure so the candidate was chosen jointly by the academics following a skype conference call with the shortlisted candidates.

For Mainz, there were two good applications. The academic in charge of Mainz chose the most relevant student for his post but sent the other good application to two other consortium members in ESPCI but it turned out that the profile of this second candidate did not match the criteria needed to apply for the post in ESPCI.

Following these publications, a total of 197 applications were received.

Regarding the gender distribution, 78% are male (153 male applications) and 22% came from female applicants (44 female applications).

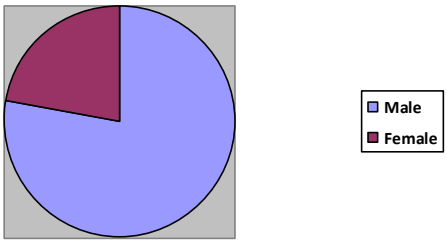


Figure 1 Gender distriburion in applications

We can say that candidates were not centralized in a part of the globe. Applications came from various countries. The country of candidates that stands out is India with a total of 57 applications, thus 29% of the total letters received. Followed by Iran with 28 candidates then by China with 19 applications.

The application distribution went like followed:

1 Application : Mexico, Marocco, Sri Lanka, Indonesia, Tunisia, Soudi Arabia, Lebano, Cameroun, Brasil, Trinité and Tobago, Portugal, Finland

2 Applications: Belgium, United Kindgom, Poland, Iceland, Denmark, Sweden

3 Applications: Russia, Malaysia, Egypt

4 Applications: Bangladesh, Greece, France

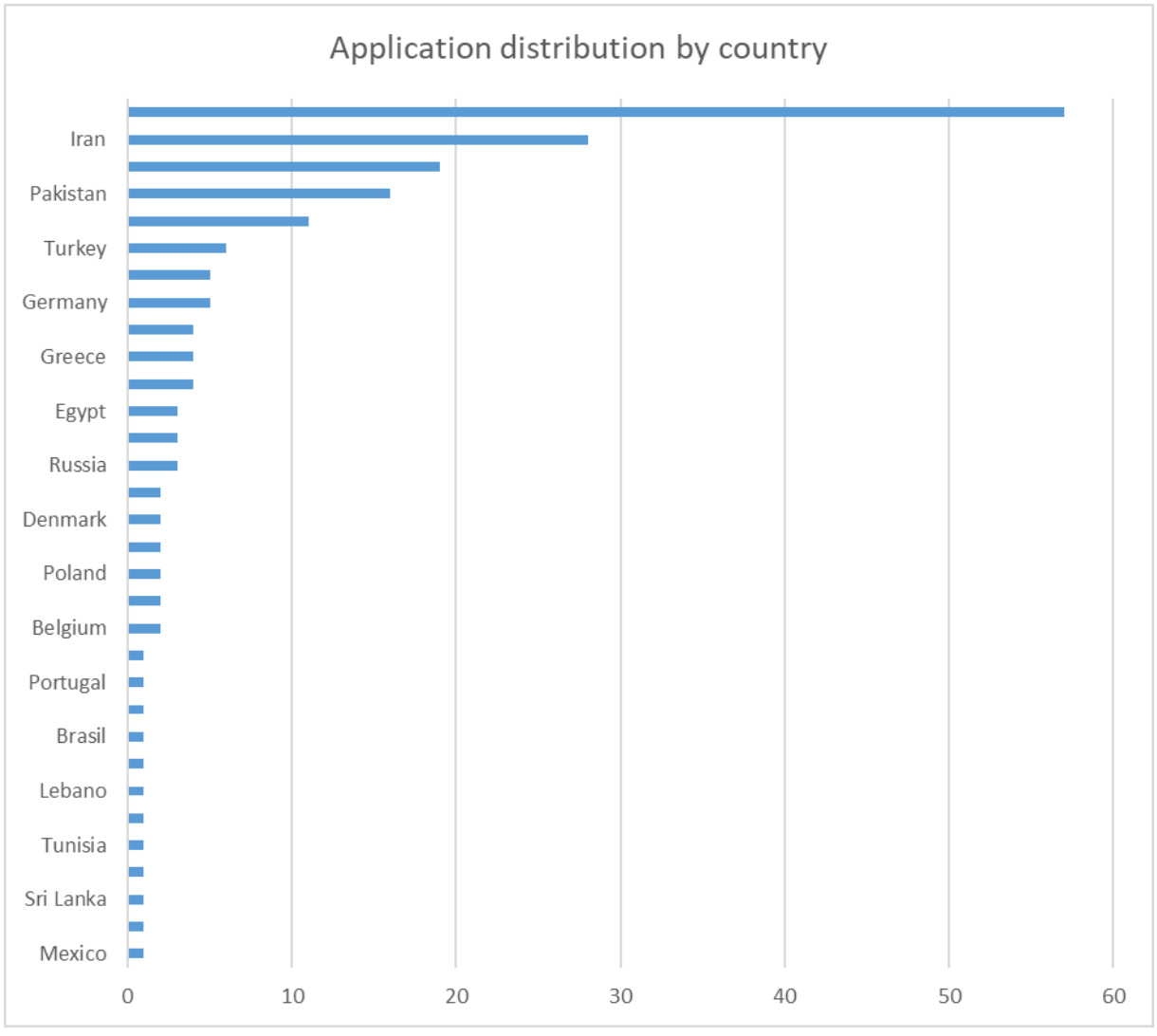
5 Applications: Germany, Spain

6 Applications: Turkey

11 Applications: Italy

16 Applications: Pakistan

Figure 2 Worldwide application distribution



Following a selection made by the supervisors in charge of each ESR, the 13 candidates below were selected.

ESR	Recruiting Participant	Joint supervision	Starting Month
ESR1 **Clément Coutouly France**	C.A. Fustin (UCL)	D. Vlassopoulos (FORTH)	March 2018
ESR2 **Rowanne Lyons Trinité et Tobago**	C.A. Fustin (UCL)	Q. Huang, O. Hassager (DTU)	September 2018
ESR3 **Larissa Hammer Germnay**	R. Nicolaÿ (ESPCI)	E. van Ruymbeke (UCL)	June 2018
ESR4 **Stefania Traettino Italy**	M. Cloitre (ESPCI)	S. Seiffert (UM)	September 2018
ESR5 **Christina Pyromali Greece**	D. Vlassopoulos (FORTH)	S. Seiffert (UM)	April 2018
ESR6 **Wendi Wang China**	Q. Huang (DTU)	G. Ianniruberto (UN)	June 2018
ESR7 **Carole-Ann Charles Belgium**	C. Ligoure (CNRS)	D. Vlassopoulos (FORTH)	January 2018
ESR8 **Consiglia Carillo Italy**	D. Vlassopoulos (FORTH)	C. Creton (ESPCI)	September 2018
ESR9 **Simone Sbrescia Italy**	P. Steeman (DSM)	E. van Ruymbeke (UCL)	May 2018
ESR10 **Paola Nicolella Italy**	S. Seiffert (UM)	C. Fustin (UCL)	September 2018
ESR11 **Hongwei Liu China**	G. Ianniruberto (UN)	O. Hassager (DTU)	September 2018
ESR12 **Yanzhao Li China**	E. van Ruymbeke (UCL)	S. Seiffert	September 2018
ESR13 **Jianzhu Ju China**	C. Creton (ESPCI)	C. Ligoure (CNRS)	September 2018

We encountered no problem in the recruitment of the candidates. ESR candidates are mainly European (strong contingency from Italy) and Chinese. We had no problem in the process to issue the visas for these students.

4. Career development plan for each recruited researcher

Each researcher received a Career Development Plan to complete during the first few weeks they started working on the project. The template of the PCDP submitted to the ESR can be found in Appendix 6. All PCDP's were collected by the project manager, they were then read and assessed by the Executive Committee members. The ESR will have to complete the form once again at the end of next year. They will be evaluated once more at the next submission period, that is to say at the end of October 2019.

5. Management of action

Structure

The management structure has been organized as proposed in the initial project plan.

As stated initially, the overall management of the network is based on **three bodies**:

A Supervisory board (Governing Board), which will effectively take all decisions. It is chaired by the coordinator, Evelyne van Ruymbeke and includes representatives of all beneficiaries as well as of the associated partners. It meets annually to approve and review decisions made by the executive committee, and discuss the progress of DoDyNet.

The members of the the Supervisory Board are:

Coordinator
Prof. E. van Ruymbeke (UCL)

Governing board
Prof. C. Creton (ESPCI)
Dr Q. Huang (DTU)
Prof. G. Ianniruberto (UN)
Prof. C. Ligoure (CNRS)
Dr. P. Roose (Allnex)
Prof. S. Seiffert (UM)
M. Seitz (DSM)
Prof. E. van Ruymbeke (UCL)
Prof. D. Vlassopoulos (FORTH)
Patrice Roose (allnex)
Stephan Zoelner (tesa)

PhD representative : Larissa Hammer (ESPCI) and Paola Nicolella (UMainz).

Each meeting is followed by a Governing Board meeting which includes academics from every institution. Following the first Governing Board Meeting in Belgium during the Kick-Off Meeting (see below), it was decided unanimously that industrial members would also be part of the Governing Board.

The researchers are also involved in this Governing Board. Indeed, it was asked that the ESR students selected two Responsible Fellows to represent them in the Governing Board meetings. Larissa Hammer (ESPCI) and Paola Nicolella (UMainz) accepted to be the first two Responsible Fellows.

An Executive committee which includes the coordinator, Evelyne van Ruymbeke and representatives of the supervisory board designated at the kick-off meeting, deal with strategic decisions such as modifications of the training program, overseeing the recruitment and PCDP of the ESRs, organizing the international meeting. Its objective is to ensure the good running of DoDyNet, and to report to the Supervisory board any issue or question which needs to be addressed. The participation of at least one industrial partner will enforce the network's commitment special attention to bridge academic research and industrial interests, towards possible applications. The committee will meet every 6 months (annual and intermediate meetings) and more often, if necessary.

The members of the Executive Committee are:

Dr. Tom Engels (DSM)
Prof. E. van Ruymbeke (UCL)
Prof. D. Vlassopoulos (FORTH)

An International Advisory Board (IAB) consisting of the visiting experts. It advises and comments annually on the progress of the ITN in research and training. It meets with the supervisory board and the other members of the consortium during the Summer School (scheduled in July 2019).

Prof. M. Rubinstein (Duke University, USA)
Prof. R. Colby (Penn State University, USA)
Prof. H. Watanabe (Kyoto Univeristy, Japan)
Prof. J. Ping Gong (Hokkaido University, Japan)
Prof. I. Voets (Eindhoven University of Technology, The Netherlands)
Prof. Z. Wang (University of Reading, United Kingdom)
Prof. D. Read (University of Leeds, United Kingdom)
Prof. B. Olsen (MIT, USA)

The three bodies are complemented by a) the **training officer** (Giovanni Ianniruberto, UN) in charge to implement our training programme; b) the **industrial liaison officer** (Paul Steeman,

DSM) who will ensure the strong industrial commitment and oversee the organization of industrial visits and workshops; c) the **dissemination officer** (Laurence Ramos, CNRS) who will coordinate the communication both within and outside the consortium; and d) the **gender officer** (Qian Huang, DTU), who will oversee all actions planned related to gender aspects. In addition, **two ESRs** will be annually elected by the ESR in order to coordinate their activities and meetings.

Information on the members of the different board, work packages leaders and advisory board are also detailed in Appendix 7.

Consortium Agreement

A consortium Agreement was drawn up and signed by all Partners. The discussions during the Kick-off meeting between different partners was a pivotal point in the decisions settled in this Consortium Agreement.

Kick-Off Meeting

The Kick-off Meeting took place in Salle du Sénat Académique (room A3.16), Halles Universitaires, in Louvain-la-Neuve (Belgium) on the 30th of November and 1st of December 2017.

The participants to the Kick-off Meeting were Costantino Creton, Tom Engels, Charles-André Fustin, Christine Hambursin, Ole Hassanger, Qian Huang, Giovanni Ianniruberto, Christian Ligoure, Bernd Lûhmann, Peter Jeppe Madsen, Tetsuharu Narita, Renaud Nicolaÿ, George Petekidis, Laurence Ramos, Patrice Roose, Sebastian Seiffert, Michelle Seitz, Paul Steeman, Dimitris Vlassopoulos, Evelyne van Ruymbeke and Bastian Wedel.

The Kick-off meeting was a very good occasion to get members to get to know each other, especially new academics to the network. It was also an excellent opportunity for industrial members to get to know the scientific team and vice versa as they are set to play a tandem role in this project.

The points addressed were the following:

Open-access to research in Horizon 2020 was presented to the members of the network and the different repositories presented. Its implementation in DoDyNet was discussed and the basis of the “Data Mangement Plan” were layed down. The members decided that as the data is essentially experimental, data will be given in the form of tables under the “.dat” format. These tables will be directly related to our publications and will be accessible to anyone who wishes to consult them.

The aim being that all the figures that appear in our publications will come with a series of tables with all the data.

The codes related to this data will not be given. Certain deliverables will essentially be under the form of computer codes. These codes will not be accessible as they are based on a number of previous years of research.

Evelyne van Ruymbeke recalled the main objectives that were determined in the final proposal. She also recalled the target applications related to these objectives and the research methodology that should be adopted.

She also recalled by who each ESR would be supervised and the duration of research and contract of each ESR. The industrial secondments for each ESR were also presented. It was reminded that any changes to the initial plan should be mentioned to the executive board (or the project coordinator).

Giovanni Ianniruberto accepted the role of Training officer. He accepted hosting the next Summer school in July 2019.

It was proposed to make an e-course on the project. The person in charge would be Michel Cloitre with the help of Renaud Nicolaÿ. The idea is to have a small course online to advertise the project and this specific scientific project.

Regarding visiting experts, it was decided that at each Governing Board meeting, the members of the board would say which visiting expert they would like to invite and see how it is possible for other members of the network to participate to the invitation or extend the invitation to another university close by. It was specified that a budget is available for punctual visits of these visiting experts. Procedures have to be set and they should be valid for all members of the network. It was also decided to invite them to our project meetings.

Training evaluation was also discussed. For certain universities like UNaples, ECTS are mandatory. It is better for them to have an evaluation at each training event and not only at the end of the project. For other universities it is not mandatory. It is then sufficient to say that they have followed the course, and it is not necessary for the students to pass an exam.

On the subject of Industrial workshops, Allnex says that with the changes happening in their company for the moment, it is difficult for them to say at this stage if they can participate actively in a worshop on Month 42 of the DoDyNet project. tesa has to confirm its participation. They asked that a one page document be drafted explaining more precisely what is expected of them in these Industrial workshops, how long they would be, what their aim was, etc.

The calendar of the following meetings was discussed with all the members as to maximize the number of members present to all the meetings.

On Dissemination : It was suggested to publish the end of project publication in the *Journal of Soft Matter*. The choice was made as this journal appeals to a large audience. The Project Manager needs to contact them to see if they would be interested in this kind of project.

Regarding the Open Access program, following the presentation done by Pierre Mersch of ADRE administration on this aspect that is new to this kind of project, time was taken to address further questions and interrogations on the subject of open access and its implementation in DoDyNet. It was decided that the articles would be accessible in their version prior to acceptance by a publication or journal. The accepted version by the journal will be published as a final unadvertised copy.

Governing Board Meeting FORTH September 2018

The first full Governing Board took place during the meeting in FORTH in September. The detailed minutes of this Governing Board meeting in Appendix 8. This meeting insured that all topics are covered and questions and issues can be talked off freely and questions answered collectively. Topics discussed vary around the following themes: the following meetings' agenda and organization planning, Industrial workshop setting and programme, assessment of training given, visiting experts to invite for lectures and in the network, budget measures and rules, gender equality issues.

Governing Board Meeting DSM January 2019

The second Governing Board took place during the meeting in DSM on the 31th of January 2019. The detailed minutes of this Governing Board meeting in Appendix 9. This meeting insured that all topics are covered and questions and issues can be talked off freely and questions answered collectively. Topics discussed vary around the following themes: next meeting in Denmark (presentation by Qian Huang), Summer School in Capri July 2019 (presentation by Giovanni Iannureberto), dates of the next meetings, feedback on the Training modules already given, Reports, Budget, Capri Workshop, Dissemination, ICR-Kyoto sponsor, Mid-Term Check content, Reporting (Milestones and Deliverables to date),Visiting experts, Secondment Discussion and Time for general questions and questions from students.

Data Management Plan

A Data Management Plan was issued in March last year (see Deliverable WP1 D.1.23 N100). As stated already, DoDyNet will have no ethical problems related to it. The only ethical aspects that could appear in this project would be related to experience protocols but these concern experiences and not the data that will be made available for consultation and re-use.

Work related Risks

Regarding risks, the subject was presented extensively in the Deliverable EPQ requirement 1 (Deliverable WP10 D.10.1 N1). For this project, it needs to be recalled that for the work undertaken, the security risks are minor. The only critical issue is the use of solvents. Thus we wanted to make sure that our ESR were taking the necessary precautionay measures. So we submitted a questionnaire to all our ESR team. The questions covered the following areas

: Do you do any experimental data? If yes, do you use solvents in these experiments? Do you work with or handle any products that could be dangerous for your health and safety? If yes, which products do you handle? What are the measures you take to protect yourself? Thus what are the safety measures taken?

The full answer to these questions, can be found in the related Deliverable (WP10 D.10.1 N1).

There were no difficulties or issues concerning the implementation of the initial work plan.

6. Dissemination and Outreach Activities

The Dissemination Work package leader is Laurence Ramos. She regularly reminds ESR of the importance of outreach activities. During each meeting, she presents the activities that have been suggested and who can be in charge.

Different communication activities were undertaken during this first working period. First, the project manager put in place the website, accessible on the following address: www.dodynet.eu.

Information on our project and on our research team can be found there.

As we are already planning our Summer School, which will take place in Capri in July next year, we also used our website to publish information on the aim of the school and its objectives. The programme, flyer are also available online. A registration form has also been created and is accessible for any external researchers interested in the topics addressed during the Summer School. There are currently 50 peoples enrolled in this event.

The project mananger also created a flyer to advertise our Summer School, topic and confirmed invited speakers. A version of the flyer can be found in Appendix 10.

Finally, following our first project meeting in FORTH Crete, we issued a Newsletter. The content of this Newsletter was done by two of our ESR, Rowanne Lyons (UCL) and Carole-Ann Charles (Université de Montepellier). The newsletter focused on different aspects: the presentation of our ESR team, a focus on the research already undertaken by the ESR who had already started working on the project, a feed-back on the meeting held in FORTH.

The Newsletter was sent to our network and to our visiting experts by mail. It is also available on our website, in the section "*News*".

You can find a version of the Newsletter in Appendix 11.

After the Advanced Modules that took place in January 2019 in DSM, another Newsletter was made by Clément Coutouly (UCL) and Simone Sbrescia (DSM). It was also sent out as the first one and published online. It can be found in Appendix 12.

During the DSM Meeting, Laurence Ramos presented the following outreach activities that will be implemented

- Creation of a Youtube channel :
    - Experimental videos by ESR
    - Videos of Poster Session : short video Q&A
    - Videos of Invited Speakers during Summer School (prepare questions in advance)
    - Videos of ESR with questions on their work

In January 2019, an Instagram account was created by our ESR, each week one student publishes a photo of his work, his experiment, his results. Publications are variable and dynamic so if a student has something interesting to post, he can of course publish at any time.

The account is : https://www.instagram.com/esr.dodynet/

In April 2019, the account has 17 publications, 41 people following its activities and 87 subscriptions to other related pages.

Our next event will be the Summer School on Transient and Complex Polymer Networks in Capri in July 2019, all our ESR will present a poster with their work.

An article was also published on DoDyNet in the *Belgian Reseach in Europe* magazine, 1st Quarter 2019, p.150.

7. Impact of the Action

The impact of the project for this period was mainly measured by the three institutions that have had ESR for the longest period of time.

For UCL, the project has already helped to:

- Start new collaborations with colleagues from UCL on Double Dynamic Networks: working on this topic, we realized that different colleagues (in particular: J.F. Gohy, A. Jonas, K. Glinel, C. Dupont) were working on the synthesis of similar systems, without having the expertise of modelling their materials. This has allowed us to start new local collaborations, in which we measure the dynamics of their systems and try to understand and model them.

- Settle a short rheology course open to all: On the request of Simone Sbrescia, we are now organizing a short rheology course (one week) based on modelling the rheological behavior of complex polymers. This course, which is open to all, will be followed by 8 people from different institutions. The objective is to share our knowledge of modelling the dynamics of Double Dynamic Networks.

FOR ESPCI, Paris, "Being part of the DoDyNet ITN allowed us to exchange with scientists having complementary expertise to ours, and to identify potential collaborations within and outside the scientific scope of DoDyNet. The recruitment of Larissa Hammer as an ESR in the DoDyNet ITN allowed our group to start working on the synthesis of double dynamic network, a key topic for us. From the practical point of view, Larissa is already playing an important role on the daily life of our team. She is very well integrated and assume responsibilities such as chemical ordering for example."

For the University of Montpellier, the recruitment of the ESR had the following impact:

- improvement of the drops impact experimental set-up for a better visualization of the expansion of the fluid sheets
- formulation test of several transient networks tests, to identify the best samples that could exhibit transient elastocapillary effects.
- formulation tests of composites transient/permanent networks and measurements of the viscoelastic properties : giving up of this topic.
- The ESR recruited, Carol-Anne, was one of the organizers of the 2018 PhD day of the Laboratoire Charles Coulomb (an annual internal scientific meeting where the PhD students of the lab present their works, it schedules around 40 talks in November this year).

FORTH University in Greece highlighted that:

The structure of DoDynet helped recruiting ESRs, who provide a high complementarity into our research group.

They both learn a lot but at the same time, they have skills that nicely complement those of other students in the group.

This allows them to integrate well and adjust fast, so they can be productive. To this end, Dodynet helps a lot with its highly interdisciplinary program.

Finally, the team in DTU, Denmark put the emphasis on the fact they had “received several excellent applications during the recruitment process, and got a highly qualified ESR. The project has enhanced collaborations between different research groups in our department, since on one hand the ESR needs to learn different techniques both experimentally and theoretically, as well as internal local support; and on the other hand the other groups are interested in the ESR's project. The training workshop (which will take place at DTU later) will provide an opportunity not only for the ESRs but also for our local students to learn the frontier knowledge in the field of soft matter. It will also provide an opportunity for the DoDyNet members to know our institution better”.

Appendix 1 : Elementary Modules I Programme

Elementary Modules I

Venue : ***IESL, FORTH (Seminar room 1)***

Agenda

24 September 2018

8.45 – 9.00	Welcome and Introduction *(Evelyne van Ruymbeke, UCLouvain*)
9.00 – 11.00	Introduction to Polymer Synthesis *(Renaud Nicolaÿ, ESPCI)*
11.00 – 11.30	*Break*
11.30 – 13.00	Introduction to supramolecular polymers *(Charles-André Fustin, UCLouvain)*
13.00 – 14.30	*Lunch*
14.30 – 15.15	Basic Polymer Science *(Daniel Read, ULeeds)*
15.15 – 15.40	*Break*
15.40 – 17.30	Curing chemistry of organic coating systems *(Patrice Roose, Allnex)*

25 September 2018

8.45 – 10.15	Introduction to scattering theory *(Daniel Read, ULeeds)*
10.15 – 10.30	*Break*
10.30 – 12.00	Introduction to Scattering Techniques *(Benoit Loppinet, FORTH)*
12.00 – 13.30	Basic molecular rheology (linear regime) *(Dimitris Vlassopoulos FORTH)*
13.30 – 14.30	*Lunch*
14.30 – 15.30	High shear *(Dimitris Vlassopoulos FORTH)*
15.30 – 16.00	*Break*
16.00 – 17.30	Introduction to extensional rheology *(Qian Huang, DTU)*

26 September 2018

9.00 – 10.00	Double Dynamic Networks: a review (*Evelyne van Ruymbeke, UCLouvain)*
10.00 – 11.30	Basic principles of coarse-grained molecular simulations *(Giovanni Ianniruberto, UN)*
11.30 – 12.00	*Break*
12.00 – 14.00	Microscopic dynamics and rheology of soft gels: computational approaches and connection to experiments *(Emanuela Del Gado, Georgetown University)*

Appendix 2 : Advanced Modules I Programme

Advanced Modules I : Mechanical Properties

Venue : ***Vaalsboroek, Vaals, 30th of January 2019***

Agenda

9.00 – 10.15	Introduction to mechanical testing of soft solid polymers Costantino Creton *(ESPCI Paris)*
10.15 – 10. 45	*Coffee break*
10.45 – 12.00	Large strain viscoelasticity in solids, fracture mechanics, elements of adhesion Costantino Creton *(ESPCI Paris)*
12.00 – 13.30	*Lunch break*
13.30 – 15.00	Small angle scattering techniques (neutrons and X-rays), examples of structure modification upon deformation Julian Oberdisse *(Université de Montpellier)*
15.00 – 15.45	Wide angle X-ray scattering upon deformation : what can we learn ? Luigi Balzano (*DSM Research*)
15.45 – 16.15	*Coffee break*
16.15 – 17.15	Fatigue and lifetime prediction strategies for polymers Tom Engels *(DSM Research)*
19.00	*Group Dinner*

Appendix 3 : Industrial Workshop Programme

Venue : ***DSM, 29th of January 2019***

Agenda

9.00 – 10.00	Welcome and Introduction DSM / DMSC
10.00 – 10.45	Product Development and application development
10.45 – 11.00	*Coffee break*
11.00 – 12.00	IP – How to read a patent
12.00 – 13.30	*Lunch with panel : Industry vs academic career*
13.30 – 14.15	Sustainability
14.15 – 14.30	*Coffee break*
14.30 – 17.00	Lab tours
17.00 -	*End of the day*
17.30	Transfer to Vaalsbroek
19.00	*Group Dinner*

Appendix 4 : Project Meeting & Mid-Term Review Programme

Project Meeting & Mid-Term Check

Date : Monday 6th of May – Tuesday 7th of May 2019

Venue : ***DTU*** **-** Technical University of Denmark - Anker Engelunds Vej 1 - 2800 Kgs. Lyngby - Denmark

Building 202 – Room : R1005

Agenda

6th of May 2019

Project Meeting

9.00 – 10.00	Lecture by **Zuowei Wang *(University of Reading, UK)***
10.00 – 10.30	*Coffee break*

Synthesis and Dynamics of reversible polymer networks based on sticky chains

10.30 – 11.00	Rheological and mechanical properties of polystyrene with hydrogen bonding and ionic bonding, Wendi Wang (DTU)
11.00 – 11.30	Rheological study of linear copolymer and dual crosslinks system, Consiglia Carillo (FORTH)
11.30 – 12.00	Design and Characterization of Novel Double Dynamic Networks (DDNs) Based on Reversible Covalent Bonds, Larissa Hammer (ESPCI)
12.00 – 12.30	Synthesis and dynamics of model supramolecular polymer networks, Clément Coutouly (UCLouvain)
12.30 – 13.00	Modeling the sticky Rouse model with periodic boundary conditions, Hongwei Liu (UN)
13.00 – 14.00	*Lunch break*

Mid-Term Check

14.00 – 14.05 **Introduction:** Short introduction by the REA Project Officer and the Project Coordinator on the purpose of the meeting.

14.05 - 14.20 **Tour de table:** All scientists-in-charge should briefly present their research team and describe their role within the network. Introduction of the Partner Organisations

14.20 - 14.40 **REA Project officer presentation**: presentation on the monitoring of project implementation, reporting and purpose of the mid-term check

14.40 – 15.20 **Coordinator's report:** Presentation of the Network and the progress covering the following aspects:

Management

- Recruitment report;
- Deliverables;
- Milestones;
- Ethical issues, if applicable;
- Management meetings (activities of the Supervisory board, etc.);
- Financial aspects (if necessary);
- Critical implementation risks and mitigation actions;
- Any proposed re-orientations of the networks' activities.
- Document management and Open Research Data, if applicable

15.20– 15.45 *Coffee break*

15.45– 17.00 **Fellows' individual presentation:** Every fellow funded by the project will present herself/himself, his background and present his/her individual research project (foreseen research, training, secondments, etc.). Scientific results are not expected in the presentations at this stage of the project *(5 min per ESR)*

Project Meeting

Structure and Mechanical properties of elastomers

17.00 – 17.30 Diffusing wave spectroscopy in elastomer fracture, Jianzhu Ju (ESPCI)

17.30 – 18.00 Soft Thermoplastic Elastomer: influence of composition and molecular weight on mechanical properties, Simone Sbrescia (DSM/UCLouvain)

7th of May 2019

Venue : ***DTU – Room : Lounge in Building 229 -For Restricted sessions: Building 229 - Room 009***

Mid-Term Check

09.00 – 10.30	**Restricted session with the fellows** *(only Project Officer and all the ESR)*
	Governing Board Meeting *(members of the Governing Board)*
10.30 – 10.45	**Restricted session** *(Meeting between the coordinator and Project Officer to discuss any issue)*
10.45 – 11.15	*Coffee break*
11.15 – 12.00	**Feedback and open discussion:** Feedback from the REA Project Officer on the output of the network so far, on possible training areas for future exploitation or the impact on fellows' future careers development ***(all members of the network)***
12.00 – 13.00	*Lunch break*

Project Meeting

13.00 – 13.30	Synthesis and dynamics of double networks based on slide-ring materials, Rowanne Lyons (UCLouvain)

Structure and Dynamics of metallo-supramolecular star polymers

13.30 – 14.00	Structure and diffusion in DDNs at the nano- to micro- scale, Paola Nicolella (UM)
14.00 – 14.30	Non Linear Viscoelastic Response Of Metallo-Supramolecular polymeric networks (in melt state), Christina Pyromali (FORTH)
14.30 – 15.00	Blend two metal-ligand crosslinks with distinct relaxation modes in telechelic star polymer, Yanzhao Li (UCLouvain)
15.00 – 15.30	*Coffee break*

Reversible gels and microgels

15.30 – 16.00	Elasto-capillary effect in double dynamic networks, Carole-Ann Charles (CNRS Montpellier)
16.00 – 16.30	Repulsive vs associative microgels, Stefania Traettino (ESPCI)
16.30 – 17.00	Question and answer session and wrap-up *(E. van Ruymbeke, UCLouvain)*

Appendix 5 : ESR open positions advertisement

Marie Sklodowska-Curie Innovative Training Networks

DoDyNet: Double dynamics for design of new responsive polymer networks and gels

Polymeric gels and networks are ubiquitous in daily life (foodstuff, cosmetics) and high-added value applications (tissue engineering, adhesives, coating, drug release, portable batteries, additive manufacturing). They can be either permanent (covalently cross-linked) and resist flow, or physical (reversible) and easy to process while creeping at long times. The grand challenge is to efficiently combine and control within the same material, distinct features of these two classes of networks, such as large mechanical strength, deformability, swelling and self-healing, in order to create multiply responsive materials for new applications.

The objective of DoDyNet is to develop a research roadmap that enhances our understanding of the synergistic effects arising by combining distinct dynamic modes within a polymeric network. These '**Double Dynamics Networks**' (DDNs) are characterized by a multi-scale viscoelastic response that can be tuned via molar mass, fraction of component and dynamics of (transient or exchangeable) bonds. This will enable us to selectively tailor their macroscopic properties at molecular level. Based on this concept, the integrated research program involves (1) novel synthesis of different DDNs; (2) detailed analysis of structure; (3) rheology and dynamics; (4) modeling and simulations; and (5) mechanical properties relevant to applications. The ESRs will benefit from the close inter-connection among these complementary tasks with the goal to obtain criteria for designing and developing new industrial DDN systems and optimizing existing materials.

DoDyNet is a highly interdisciplinary and inter-sectorial project, the groups involved are world-leaders in their fields, and the tasks strategically designed to ensure strong synergies. It offers young researchers an extraordinarily diverse training platform with a deep grasp of soft matter and unique exposure to industrial environment, needed to address emerging scientific and technological challenges.

Applications should be sent by email (a single pdf file containing a detailed CV, a transcript of marks obtained during the Master, a motivation letter, and the names of two referees) to:

dodynet-manager@uclouvain.be

The applicant has to clearly indicate the number of the project(s) for which he/she is applying.

Starting dates: between November 2017 and June 2018.

Project duration: 36 Months. (48 Months for ESR1, ESR2, ESR9 and ESR12).

ESR1: Synthesis and dynamics of model double networks based on supramolecular polymer

Location: UCL, Louvain-La-Neuve, Belgium
Supervisors: C.A. Fustin (Charles-andre.fustin@uclouvain.be) and E. van Ruymbeke (evelyne.vanruymbeke@uclouvain.be)

The aim of this PhD thesis is to study double networks based exclusively on supramolecular interactions. The work will consist in synthesizing building blocks (functionalized initiator or monomers) and polymers of controlled architecture bearing functional groups at well-defined locations. The latter will be mainly done by controlled radical polymerization and polymer post-modification. Supramolecular double networks will then be prepared and their rheological properties will be investigated in detail by various techniques (shear rheology, extensional rheology…) to probe the dynamics of these systems.

For this project, a **solid background in polymer chemistry is mandatory**. Good knowledge in organic chemistry and/or supramolecular chemistry is a plus. The student will have access to the doctoral training offered at UCL and to the expertise developed in the institute on soft matter materials (see https://uclouvain.be/en/research-institutes/imcn/bsma)

ESR2: Synthesis and dynamics of double networks based on slide-ring gels

Location: UCL, Louvain-La-Neuve, Belgium
Supervisors: C.A. Fustin (Charles-andre.fustin@uclouvain.be) and E. van Ruymbeke (evelyne.vanruymbeke@uclouvain.be)

The aim of this PhD thesis is to study hybrid double networks based on slide-ring gels and supramolecular interactions. The work will consist in synthesizing building blocks (functionalized initiator or monomers, macrocycles,…) and polymers of controlled architecture bearing functional groups at well-defined locations. Double networks will then be prepared and their rheological properties will be investigated in detail by various techniques (shear rheology, extensional rheology, etc.) to probe the dynamics of these systems.

For this project, a **solid background in polymer chemistry and organic chemistry is mandatory**. Good knowledge in supramolecular chemistry is a plus. The student will have access to the doctoral training offered at UCL and to the expertise developed in the institute on soft matter materials (see https://uclouvain.be/en/research-institutes/imcn/bsma).

ESR3: Synthesis and structure of reversible covalent double dynamics networks

Location: ESPCI, Paris, France
Supervisor: R. Nicolay (renaud.nicolay@espci.fr)

The goal of this PhD project is to design and prepare double networks that will contain both reversible chemical crosslinks, *i.e.* crosslinks that can be broken and reformed on demand, and dynamic chemical crosslinks, *i.e.* crosslinks that can exchange the chemical fragments they connect without any loss of connectivity. These networks will be prepared by controlled radical polymerization and/or chemical modification. The effect of the topology of the

polymers, of their functionality and of the dynamics of the reversible and dynamic crosslinks, on the rheological and mechanical properties of the gels will be investigated. In collaboration with partners of the ITN, the structure and homogeneity of the networks will be studied by scattering and microscopy techniques, and the networks will be used as model objects to model the rheological features of double dynamic networks.

The PhD candidate should possess a solid background in polymer chemistry. Acquaintance with physical-chemistry and/or physics of polymers would be a real advantage. The student will have access to the doctoral training of Paris Science et Lettres Research University and will benefit from the highly interdisciplinary environment of ESPCI Paris.

ESR4: Synthesis and properties of responsive hydrogels based on reversible covalent chemistry

Location: ESPCI, Paris, France
Supervisors: R. Nicolay (renaud.nicolay@espci.fr) and M. Cloitre (michel.cloitre@espci.fr)

The PhD student will be at ESPCI working on the synthesis and properties of highly swellable DDNs based on reversible covalent bonds, in relation with their structural information.

The applicant must have a strong background in polymer chemistry, as well as in polymer physics. The student will have access to the doctoral training of Paris Science et Lettres Research University and will benefit from the highly interdisciplinary environment of ESPCI Paris.

ESR 5: Viscoelastic response of double dynamics polymer networks under large shear deformation

Location: IESL – FORTH, Heraklion, Crete, Greece
Supervisor: Dimitris Vlassopoulos (dvlasso@iesl.forth.gr).

Systematic study of the linear and nonlinear viscoelastic response in shear of specially synthesized double dynamics polymer networks. The emphasis is to relate molecular characteristics of these networks to their macroscopic response. To this end, additional dynamic light scattering are planned, whereas collaboration with UM (e.g., fluorescence correlation spectroscopy) and UCL (e.g., modeling) is envisaged. In addition, further interactions with DTU and ESPCI are possible.

Target at end of PhD: skills toward molecular design of complex soft materials with desired properties, molecular rheology and dynamics, soft matter physics.

A solid background in thermodynamics and transport phenomena is desired. Acquaintance with rheology and/or light scattering is a plus. Hence, a degree in chemical engineering or physics or materials science seems appropriate albeit not mandatory.

FORTH offers a highly interdisciplinary, stimulating environment with many visitors and exchange scientists, and a cost-effective life in beautiful Crete.

ESR6: Viscoelastic Response of Double Dynamics Polymer Networks under Transient Elongation

Location: The Danish Polymer Centre, DTU, Copenhagen, Denmark
Supervisors: Dr. Qian Huang (qh@kt.dtu.dk), Prof. Anne Ladegaard Skov (al@kt.dtu.dk), Prof. Ole Hassager (oh@kt.dtu.dk)

The objective of this PhD project is to understand the exact role of molecular parameters such as entanglements, dangling ends and chain architectures on the dynamics of Double Dynamics Networks (DDNs). The project will focus on studying the nonlinear extensional rheology of different DDNs. In order to relate the rheological results to mechanical properties towards applications, the fracture behavior of DDNs in tensile mode will also be investigated.

Responsibilities and tasks:

- Study the nonlinear extensional behavior of the model DDNs as a function of their composition. Nonlinear rheological measurements will be performed under controlled uniaxial extension by using the state-of-the-art filament stretching rheometer (FSR) at DTU.
- Relate the nonlinear extensional properties to nonlinear shear behavior (in collaboration with FORTH).
- Extract the main structure parameters which influence their extensional properties (in collaboration with University of Naples)
- Investigate the strain hardening properties and fracture mechanisms under elongation. Fracture will be investigated by coupling the FSR with a high-speed camera at DTU.
- Relate the strain hardening and fracture to their mechanical properties (in collaboration with ESPCI).
- Relate the extensional properties to the application of adhesion (in collaboration with TESA, where an industrial secondment is planned).

Qualifications: Candidates should have a master's degree in material science, physics, or engineering or a similar degree with an academic level equivalent to the master's degree in engineering. Experimental experience of polymer rheology is an advantage.

Approval and Enrollment: The scholarships for the PhD degree are subject to academic approval, and the candidates will be enrolled in one of the general degree programmes of DTU. For information about the general requirements for enrolment and the general planning of the scholarship studies, please see the DTU PhD Guide.

We offer an interesting and challenging job in an international environment focusing on education, research, scientific advice and innovation, which contribute to enhancing the economy and improving social welfare. We strive for academic excellence, collegial respect and freedom tempered by responsibility. The Technical University of Denmark (DTU) is a leading technical university in northern Europe and benchmarks with the best universities in the world.

ESR7: Opening for an experimental PhD position "Elasto-capillarity in associative polymer networks"

Location: CNRS & University of Montpellier, France
Supervisors: Christian Ligoure (Christian.ligoure@umontpellier.fr), and Laurence Ramos (Laurence.ramos@ umontpellier.fr).

The goal of this project is to understand and rationalize how relaxation dynamics in transient polymer networks impact elasto-capillary effects. Elasto-capillarity, which involves a competition between the bulk elastic strain energy and the surface energy, is relevant at macroscopic scales only for ultra-soft solids (with Young modulus < 100 Pa) and dramatically affects the shape, dynamics and failure of a soft solid material. We will experimentally investigate single dynamics polymer networks (SDN) and double dynamics polymer networks (DDN). We expect drastically different and original behavior for DDNs, which should strongly vary with the lifetime and/or elastic modulus of each constituting network.

Several experimental approaches will be developed to investigate those effects, including the impact of a drop of SDN and DDN on a solid surface, the suction and indentation of SDN and DDN, and the frequency-dependent elasticity of a solid with SDN and DDN inclusions.

The successful candidate will have a good background in soft matter physics or material science. Salary and benefits will be according to the EU rules.

ESR 8: Deformability and fracture mechanisms in reversible covalent DDNs

Location: IESL – FORTH, Heraklion, Crete, Greece
Supervisor: Dimitris Vlassopoulos (dvlasso@iesl.forth.gr).

Systematic study of the nonlinear shear rheology of specially synthesized reversible covalent double dynamics networks having different characteristics. It involves using special tools developed in-house. A combination with selective dynamic light scattering and in-situ light or neutron scattering (in facilities) is planned. Linking rheological instabilities with visual observations of the sample and velocity profiles (relevant setups to be developed) will provide insights. Close interaction (and joint experiments via exchange visits) with ESPCI (e.g., velocity measurements, fracture), CNRS (e.g., fracture) and DTU (e.g., extensional rheology) are foreseen. Data analysis and model development/manipulation is also planned.

Target at end of PhD: skills toward molecular design of complex soft materials with desired properties, molecular rheology, rheo-physics, soft matter physics.

A solid background in thermodynamics and transport phenomena is desired. Acquaintance with rheology and/or light scattering is a plus. Hence, a degree in chemical engineering or physics or materials science seems appropriate albeit not mandatory.

FORTH offers a highly interdisciplinary, stimulating environment with many visitors and exchange scientists, and a cost-effective life in beautiful Crete.

ESR 9: Influence of the composition on the mechanical properties of thermoplastic DD elastomers

Location: DSM, Geleen, The Netherlands
Supervisors: Michelle Seitz (Michelle.Seitz@dsm.com), Evelyne van Ruymbeke (evelyne.vanruymbeke@uclouvain.be)

In this project, the student will begin by exploring structure-mechanical property relationships for a model class of semi-crystalline TPEs by systematically varying parameters (e.g. molecular weight, hardblock length and distribution, and entanglement densitry) and conducting well-defined mechanical experiments as a function of temperature or rate. Based on this understanding of mechanims for TPEs, the student will explore to what extent adding additional dynamics (e.g. combination of types of physical crosslinks, covalent bonds, or via crystal morphology) can improve these key mechanical properties. In the second part of the PhD project, the student will utilize the experience gained by studying the model system(s) to contribute to characterizing the complex response of the dual dynamic network systems that are developed within context of the grant's academic network and to translate these concepts into industrial practice. A combination of mechancial testing and structural analysis is foreseen as well as a connection to polymer physics – emphasis will be on generating wholistic, mechanistic understanding of the experimental observations.

The candidation **must have a solid background in materials science and affinity for experimental work** with a strong link towards mechanistic understanding (previous degrees could be in mechanical or chemical engineering, applied physics, polymer physics or chemistry, or materials science).

The student will be located for the first three years at DSM's Material Science Center, the shared research unit of > 300 people support the Materials Science Cluster within Royal DSM with expertises ranging from chemistry, process technology, characterization, and engineering and physics. This in-depth exposure to high level research in an industrial, application driven environment coupled to the full DoDyNet academic network and the final year at the Université catholique de Louvain offers a unique training opportunity spanning industry and academia.

ESR10: Structure and diffusion in DDNs at the nano- to micro- scale

Location: Johannes Gutenberg-University Mainz, Germany

Supervisor: Prof. Dr. Sebastian Seiffert (sebastian.seiffert@uni-mainz.de)

The principal motivation of the DoDyNet European research initiative is to study and develop double-dynamic networks with outstanding mechanical properties. These properties, in turn, are coupled to the polymer-network topologies and architectures, which therefore mandates these to be characterized on two length scales: that of the network mesh sizes on scales of 1–10 nm, and that of topological inhomogeneities on scales of 10–1000 nm. In this workpackage, these nano- to microstructures shall be assessed by mutually synergistic use of scattering and fluorescence-microscopy techniques, encompassing static and dynamic light scattering, partially supplemented by small angle neutron and x-ray scattering, as well

as confocal-microscopy based fluorescence correlation spectroscopy and fluorescence photo-bleaching recovery.

Expertise required by the candidate: Master degree in chemistry, physics, or polymer science, with a special strength in physical chemistry; Experimental experience with polymer sample preparation and methodology such as light scattering and optical spectroscopies, ideally fluorescence spectroscopy

Benefits for the candidate other than Marie Curie compensation: Potential enrollment into the Mainz Graduate School of Excellence “Materials Science in Mainz”

ESR11: Modeling the nonlinear rheology of reversible double dynamics networks

Location: UN, Napoli, Italy
Supervisor: G. Iannirubertо (iannirub@unina.it)

The research project aims at understanding the molecular origin of the nonlinear shear and extensional behavior of the double dynamics networks by rationalizing the influence of structure parameters on nonlinear dynamics. The work will consist in extending successful kinetic models for simple networks and/or entangled polymers to double networks. The approach will be twofold, encompassing both molecularly-based constitutive equations and stochastic mesoscopic simulations, coarse-grained to the level of the smaller mesh size of the double network. Though combining ingredients of supramolecular systems with entanglement effects, constitutive equations should be simple enough for possible use in numerical codes for processing simulations. As regards simulations, entanglements will be represented as slip-links joining chains in pairs and through which chains slide in their longitudinal motion (reptation). Molecular models should account for several nonlinear effects: (i) chain stretch, possibly reducing the lifetime of transient bonds, (ii) non-Gaussian effects, determining strain hardening behavior, (iii) separation of chain stretch from chain orientation due to topological constraints (typically observed in entangled systems, while normally ignored in models of crosslinked networks).

Candidates with a background in chemical engineering, materials science or physics are encouraged to apply. Good background in modeling is also a plus. The student will have access to the PhD program at UN, and hence he is expected to get the PhD degree at UN.

ESR12: Modeling the linear rheology of reversible Double Dynamics Networks

Location: UCL, Louvain-La-Neuve, Belgium
Supervisor: E. van Ruymbeke (evelyne.vanruymbeke@uclouvain.be)

The objective of this PhD project is to develop a model based on the tube theory as well as on the existing network theories, in order to describe the viscoelastic response of the supramolecular networks which combine entanglements and supramolecular dynamics. This project can be seen as the continuation of our present work on modelling the rheological behavior of end-functionalized entangled polymers.

Candidates should have a master's degree in material science, physics, or engineering. The applicant should have a good expertise in modeling as well as a good background in polymer physics.

ESR13: Application properties of double dynamics polymer networks

Location: ESPCI, Paris, France
Supervisor: C. Creton (Costantino.Creton@espci.fr)

The project will focus on the application (tensile and adhesive) properties of Double Dynamics Networks, and relate these properties to their rheological./mechanical response.

The applicant **must have a solid background in materials science and affinity for experimental work** with a strong link towards mechanistic understanding (previous degrees could be in mechanical or chemical engineering, applied physics, polymer physics or chemistry, or materials science).

Appendix 6 : PCDP sent to ESR – Assessment Year 1

Career Development Plan

Guidance on some of the competencies expected

The career development plan is divided into 3 parts. The first part (Year 1) should be completed soon after starting the position. The second part (mid-term) should be completed half way through your project. The final part (final year) should be completed near the start of your final year on the project.
Each part should be sent to the Executive Committee for approval.

The following points are a non-exhaustive series of aspects that could be covered by the career development plan, and it is relevant to the short-term objectives that will be set by the researcher and the reviewer at the beginning of the fellowship period. The objectives should be set with respect to the skills and experience that each researcher should acquire at a given time of his/her career. A postgraduate researcher at PhD level will have very different needs compared to a post-doctoral researcher at an advanced stage of his/her professional development. These objectives should be revised at the end of the fellowship and should be used as a pro-active monitoring of progress in the researcher's career.

RESEARCH RESULTS.

These should give an overview of the main direct results obtained as a consequence of the research carried out during the training period. It may include publications, conference, workshop attendance, courses, and /or seminar presentations, patents etc. This will vary according to the area of research and the type of results most common to each field. The information at this level should be relatively general since the career development plan does not strictly constitute a report on the scientific results achieved.

RESEARCH SKILLS AND TECHNIQUES ACQUIRED.

Competence in experimental design, quantitative and qualitative methods, relevant research methodologies, data capture, statistics, analytical skills.
Original, independent and critical thinking.
Critical analysis and evaluation of one's findings and those of others
Acquisition of new expertise in areas and techniques related to the researcher's field and adequate understanding their appropriate application
Foresight and technology transfer, grasp of ethics and appreciation of IPPR.

RESEARCH MANAGEMENT.

Ability to successfully identify and secure possible sources of funding for personal and team research as appropriate.

Project management skills relating to proposals and tenders work programming, supervision, deadlines and delivery, negotiation with funders, financial planning, and resource management.

Skills appropriate to working with others and in teams and in teambuilding.

TRANSFERABLE SKILLS.

Personal presentation skills, poster presentations, skills in writing reports and preparing academic papers and books.
To be able to defend research outcomes at seminars, conferences, etc.
Contribute to promote public understanding of one's own field (presentations at open days / schools / other public events, production of dissemination materials).
Other skills such as language skills, teamwork, project management, event organisation

OTHER PROFESSIONAL TRAINING (COURSE WORK, TEACHING ACTIVITY):

Involvement in teaching, supervision or mentoring

ANTICIPATED NETWORKING OPPORTUNITIES.

Develop/maintain co-operative networks and working relationships as appropriate with supervisor/peers/colleagues within the institution and the wider research community. Include details of industrial secondments, visits to other institutions.

OTHER ACTIVITIES (COMMUNITY, ETC) WITH PROFESSIONAL RELEVANCE.

Issues related with career management, management of own career progression, ways to develop employability, awareness of what potential employers are looking for when considering CV applications etc.

Career Development Plan Year 1

Name of fellow:

Department:

Institution:

Name of Supervisor:

Please read the notes at the beginning of this document for guidelines on how to complete each section.

BRIEF OVERVIEW OF RESEARCH PROJECT

1. Brief overview of Research Project, and major accomplishments/outcomes expected:

2. Milestones, deliverables, other reports linked to this project (include expected date of delivery):

LONG-TERM CAREER OBJECTIVES (OVER 4 YEARS)

1. Goals:

2. What further research activity or other training is needed to attain these goals?

SHORT-TERM OBJECTIVES (1-2 YEARS)

1. Research results *(optional for ESRs)*
    - Anticipated publications:

    - Anticipated conference, workshop attendance, courses, and /or seminar presentations:

2. Research Skills and techniques:
    - Desired training in specific new areas, or technical expertise etc:

3. Desired transferable skills:
    - Communication skills:

    - Other skills:

4. Other professional training anticipated (e.g., teaching activity):

5. Anticipated networking opportunities:

6. Grant management: *(optional for ESRs)*
    - Fellowship or other funding applications planned (indicate name of award if known; include fellowships with entire funding periods, grants written/applied for/received, professional society presentation awards or travel awards, etc.)

7. **ECTS/other university requirements:** List of identified courses / training events / activities that will contribute to any university requirements (such as ECTS credits. *This will differ from institution to institution. Please also indicate what requirements your university has (e.g. no requirements, x number of ECTS credits, x number of courses etc.)*

Date & Signature of fellows **Date & Signature of supervisor:**

Appendix 7 : DoDyNet Supervisory Board of the network

Governing board

Coordinator: Prof. E. van Ruymbeke (UCL)

Prof. C. Creton (ESPCI)

Dr Q. Huang (DTU)

Prof. G. Ianniruberto (UN)

Prof. C. Ligoure (CNRS)

Dr. P. Roose (Allnex)

Prof. S. Seiffert (UM)

M. Seitz (DSM)

Prof. D. Vlassopoulos (FORTH)

Executive committee

Dr. Tom Engels (DSM)

Prof. E. van Ruymbeke (UCL)

Prof. D. Vlassopoulos (FORTH)

Specific leaders

Dissemination officer: Prof. L. Ramos (CNRS)

Gender officer: Dr Q. Huang (DTU)

Industrial officer: Prof. P. Steeman (DSM)

Training officer: Prof. G. Ianniruberto (UN)

WP Leaders

WP 0 : Prof. E. van Ruymbeke (UCL)

WP 1: Prof. C.A. Fustin (UCL)

WP 2: Prof. S. Seiffert (UM)

WP 3: Prof. D. Vlassopoulos (FORTH)

WP 4: Prof. E. van Ruymbeke (UCL)

WP 5 : Prof. C. Creton (ESPCI)

WP 6 : Prof. Ianniruberto (UN)

WP 7 : Prof. P. Steeman (DSM)

WP 8 : Prof. L. Ramos (CNRS)

External advisory board

Prof. M. Rubinstein (University of North Carolina)

Prof. R. Colby (Penn State University)

Prof. H. Watanabe (Kyoto Univeristy)

Prof. J. Ping Gong (Hokkaido University)

Prof. I. Voets (Eindhoven University of Technology)

Prof. Z. Wang (University of Reading)

Prof. D. Read (University of Leeds)

Prof. B. Olsen (MIT)

Appendix 8: Minutes of the Governing Board Meeting, FORTH, September 2018

Venue : Seminar room 2, ITE, FORTH, Heraklion, Crete

Participants present : Charles-André Fustin, Christine Hambursin, Larissa Hammer, Qian Huang, Giovanni Ianniruberto, Christian Ligoure, Benoît Loppinet, Giuseppe Marrucci, Tetsuharu Narita, Renaud Nicolaÿ, Paola Nicolella, George Petekidis, Laurence Ramos, Patrice Roose, Michelle Seitz, Evelyne van Ruymbeke, Dimitris Vlassopoulos, Stephan Zoellner.

Governing Board Meeting

It was asked that the ESR students choose two Responsible Fellows to represent them in the Governing Board meeting. Larissa Hammer (ESPCI) and Paola Nicolella (UMainz) accepted to be the first to Responsible Fellows.

- **Meetings**

Michelle Seitz started by presenting how the organization of the next meeting was going. She underlined two points: which students would benefit from an Industrial stay and which visiting experts to invite.

For the Industrial workshop, she presented different subjects. All the points would fit in one day. Writing a CV would be a thematic that would be a bit early to present, it might be better to do this during the tesa meeting later. Visiting facilities is logistically difficult so it will be limited to certain areas.

Costantino Creton will organize the Advanced Modules, Tom Engels or Michelle Seitz can talk about different mechanical properties.

The Project Meeting would start with the Project Officer with the assessment

On the Friday, most of the students would present their results.

Who would be the best visiting expert to invite to this meeting?

Ralph Colby will be in Zurich in February so we can ask him. Ilja Voets would be logistically easier, but not ideal with the topic of the meeting but it would be a nice opportunity to meet her. Evelyne van Ruymbeke will contact them both after the meeting to see who is interested.

The budget of the event will depend on how many people will come to stay and how many nights will be booked at the venue.

For the DTU Modules, we could follow a similar structure as the one organized during Supolen. Qian Huang need to let us know if she needs help or if they want someone else to be invited or involved, even if the person is not in the network. The accommodation for this event needs to be studied quite quickly.

- **Regarding the assessment of the Training Modules**

Student assessment depends on who needs to have ECTs for their PhD Students. In UCLouvain, it is sufficient for the ESR to follow the courses. The students from ESPCI Paris, DTU, FORTH, UMontpellier do not need an evaluation either to obtain the ECTs.

The situation needs to be clarified for the University of Naples. During the Supolen project, questions were sent after the Training Modules and the students had to read papers after the meeting. The solution offered is to do a special attendance certificate for the UNaples student which specifies the courses followed during the Modules, the professors teaching and the number of hours per course.

There also needs to be an assessment of the Training Modules by the students. The answers need to be anonymous. It is decided that the questionnaire will be sent to the two Responsible Fellows so they can forward them via the ESR mailing list to the other students. Once they have answered, they will send the questionnaire to the project manager.

The feed-back from the questionnaire will be put on the website.

There is a new questionnaire that has been created for the project (*see Appendix*). The project manager will send it to the Training Officer, once it has been validated by him it will be sent to the students.

- **Visiting experts**

The objective is to invite one visiting expert at each meeting, it is a good way of keeping in contact with them. As Daniel Read is geographically close to the network, we can offer him to come everything time. He is also relevant in terms of content for the subjects which will be addressed in DTU.

For the DSM meeting, we can suggest that the invited visiting expert does a presentation of his/her work or a lecture.

For the meeting in DTU, Zuowei Wang and Daniel Read would be good people to contact as their work is related to extensional rheology.

There is also the possibility for the visiting experts to come during the project to visit the labs. It would be interesting to combine different lab visits successively.

- **Budget**

If the organization of meeting seems to be running over the amount assigned for the meeting, it has to be justified to the Governing Board.

If we can pay expenses directly from UCL, it makes it more easy on the accountant's side.

If the expenses are higher than 8 500€ for one type of expense, then an open market has to be carried out.

We will prepare a form which can be used for different expenses: travelling, sample preparation, etc.

If there is money left at the end of the project, it will be redistributed to the partners.

The Governing Board expenses are usually limited to the dinner related to this meeting. The Mid-Term Review will be put on Management. There is no overhead anymore on expenses.

The accommodation for the academics and students are covered, if there is an external invited guest then it has to be discussed during the Governing Board Meeting.

The use of a per diem following the way we work for this project is questionable as most of the expenses are already covered. This makes the per diem usually to high compared to the real individual cost of participation.

We need to cover the expenses of visiting experts and external people who participate to meetings. If we provide breakfast and lunch, then it is only the evening meal that will need to be reimbursed.

Thus the per diem of 50€ was fixed when only food needs to be payed personally and when accommodation is covered by the organization of the meeting.

Questions related to the budget

If we have external students coming, how do we estimate the cost? It will be calculated on the actual expenses. Notably for Capri which will be advertised to a broader public.

We should start advertising quite soon for the Summer School. We need to do a Mailing list and flyer to advertise it. To do this, we need information on who will be participating. Once we know this, we can send it to the Dissemination Officer, Laurence Ramos. First, we need to advertise to our network as the maximum people registered will be around 80.

- **Gender equality**

How to deal with members who need to travel with their children to attend meeetings. It is underlined that it would be preferable to avoid having meetings planned during the week-ends. The only other meeting with a weekend will be Capri as it will be held from the Monday to the Saturday.

How do we determine a limit amount to costs and respect Gender Equality? For this meeting, the cost of travel for the children was covered but nothing else. The people who organize the meeting underline that childcare can be organized but the question of the language would be problematic.

The gender equality measures are relevant for everyone, ESR included.

- **Achieved Deliverables & Milestones**

The deliverables are presented. The next due deliverable is the Yearly ESR Progress Report. The students need to make a small description of what they have done up to now. The period covered is from the start of the project to this date. The template will be made available on the website. An email will also be sent to all the students to give them the information.

Most of the Milestones regard sharing the samples. Members of the network need to inform the Project Manager is they send samples to another partner so that the information can be shared with all the network on the work that is being carried out.

Appendix 9: Minutes of the Governing Board Meeting, DSM, January 2019

Governing Board Meeting DSM 31 January 2019

Venue : DSM, Geleen in Kasteel Vaalsbroek, Vaals, The Netherlands

Participants present : Consiglia Carillo, Carole-Ann Charles, Clément Coutouly, Costantino Creton, Tom Engels, Charles-André Fustin, Sina Ghiassinejad, Christine Hambursin, Larissa Hammer, Céline Hannecart, Qian Huang, Giovanni Ianniruberto, Jianzhu Ju, Yanzhao Li, Hongwei Liu, Rowanne Lyons, Renaud Nicolaÿ, Paola Nicolella, Christina Pyromali, Laurence Ramos, Patrice Roose, Simone Sbrescia, Sebastian Seiffert, Michelle Seitz, Lars Sonnenberg, Paul Steeman, Stefania Traettino, Evelyne van Ruymbeke, Dimitris Vlassopoulos, Wendi Wang, Stephan Zoellner.

Following Meetings

- **DTU : Qian Huang**

Qian did a presentation regarding the next meeting that will take place. She presented the university's situations, the two hotels that had been chosen. She also showed the provisional budget that was expected for this meeting.

The content of the courses for the Advanced Modules II was discussed. Giovanni Ianniruberto accepted to give lectures during these Modules as his topics of research are connected to the topic presented by Qian. This, it was decided that the courses would be distributed between Ole Hassager (DTU) and Giovanni Ianniruberto (UN). The lab experiments will be taken in charge by Qian Huang (DTU).

- **Summer School Capri : Giovanni Ianniruberto**

Giovanni presented the programme for the Summer School and the visiting experts that have accepted to present a lecture during the Summer School. The venue was also presented. A provisional budget was at this stage just highlighted.

Giovanni reminded members of the Network to register to the Summer School via the registration form that is on the DoDyNet website. He also encouraged members to book their accommodation quickly as the Summer School will take place in July 2019, which is a peak season.

- **Next events?**

The dates of the next meetings were discussed. Two options were highlighted depending on if the presence of a member of the European Commission would be necessary for another assessment. If the Project Officer needs to carry out a Mid-Term Review then the Intermediate Meeting III would take place in Mainz in January 2020, the meeting in Montpellier, Annual Meeting III would have to take place in June or July 2020. If we do not need to take into account the attendance of a project Officer from Europe then the meeting in Mainz can be planned in April 2020 and the meeting in Montpellier can take place in September 2020. Members of the Governing Board prefer this second option. Christine Hambursin will contact the project Officer and see which option will suit her schedule best and if she needs to do another assessment of the project.

There is also a Workshop, organized jointly with SoftComp and ICR, that will take place in July in Capri, after the Summer School. The programme still has to be finalized. DoDyNet members can also participate and have to register online. Christine will create a new section on the website with information on this Workshop.

Training

- **Elementary Modules I**

The feed-back on the Elementary Modules was presented to the members of the board.

It was said that students positively viewed : the schedule and programme of the events, their timing, the lab visits organized, the information given on the event, the content of the courses given, the length of the courses, the choice of visiting experts and the possibility that was given of Q&A time after the courses.

The additional comments that are interesting to take into account for futher events are : having better access to course material beforehand if possible (slides in advance or course online before the presentation), having short abstract of each course in advance, having the slides on the Intranet accessible quickly. Students would appreciate the opportunity to have “hands-on practices” and “experiments” during the Modules.

- **Report**

It was also shown were the Training Reports were on our Intranet website. As well as the Yearly ESR Progress Report for the first year and the Progress Report that would be the basis of the Mid-Term Check in May 2019.

Budget

- **Up to now**

An update of the budget up to know was presented.

Management Budget	
Kick-off	4193,2€
FORTH	2075,8€
Total	6269€

Training Budget	
FORTH	12 455€
DSM	20 199,96€
Total	32 654,96€

The general distribution of the Global Training budget was recalled.

Research Training	1250€ per PM	
Associate partners		60 000€
Smaller events	15000 each, 4	60 000€
Industrial events	20 000 each, 2	40 000€
Larger events	35 000, each 2	70 000€
Online courses		4000€
Dissemination		3000€
External experts		20 400€
Total		257 400€

An estimate of the budget for the DSM meeting was also shown with a total of 20 199,96€ which sticks to the amount allocated for this type of event.

Item	
Catering (Lunch and coffee breaks) Evening Dinner + accommodation Kasteel Vaalsbroek	18 421,28€
Hotel students 28/02	1281,18€
Travel expenses course lecture Oberdisse	
Visiting expert travel expenses (Colby)	
Bags - mugs	497,50€
Total	20 199,96€

- **Capri workshop**

Evelyne asked members of the Governing Board if DoDyNet could sponsor the event with 5000€ for organization. DoDyNet members would not be asked a registration fee to participate. Members accepted this idea.

It was also decided that hotel expenses for invited speakers would be taken in charge until Sunday 28 July 2019.

Dissemination activities

Laurence Ramos presented the different activities discussed with the students. 2 ESR have been elected by their fellows to take in charge the next Newsletter. This time Clément Coutouly (UCL) and Simone Sbrescia (DSM) will work on the content of the Newsletter on the DSM event.

It was decided by ESR to create an Instagram account were they could post photos and videos of their work. To make sure the account was regularly up dated with information, it was asked that Christine makes an agenda for each ESR to have a week to publish something on the account. Of course, the idea is for the account to be dynamic so if they have something interesting to publish, they can upload news on the account when they find it appropriate.

ICR-Kyoto

Evelyne van Ruymbeke asked members of the network if ICR of Kyoto would participate to DoDyNet. They would like to make a donation to the network. The amount still has to be confirmed. Members of the network agree on this. We also need to ask them if they would like more students to attend the Summer School.

It was also suggested that a Youtube channel was created with the following :

- Experimental videos by ESR
- Videos of Poster Session : short video Q&A
- Videos of Invited Speakers during Summer School (prepare questions in advance)
- Videos of ESR with questions on their work

Mid-Term Check

A short reminder of the Mid-Term Check and its content was presented (see slides) to make sure all members had information on what was going to be discussed in May.

Reporting

A table with all the Deliverables handed in up to date was presented. The following deliverables were underlined as interesting to read before the Mid-Term Check in May.

Training Report I

- Elementary Modules I : Programme, lecturers and courses given
- Elementary Modules I : Assessment by students (practical organization and content of the courses, points to take into consideration for next course Modules)

Yearly ESR Progress Report

- Work Summary for the period
- Deliverables & Milestones
- Publications & conferences
- Courses followed
- Exchange visits

Visiting experts

It was asked if any visits of experts of our advisory board were planned in an institution. If such visits are planned, it is interesting to give the information to other members of the networks so visits can be jointly organized. For the next meeting, Zuowei Wang of Reading University will come to give a lecture. All members of our Advisory Board will be present for our Summer School.

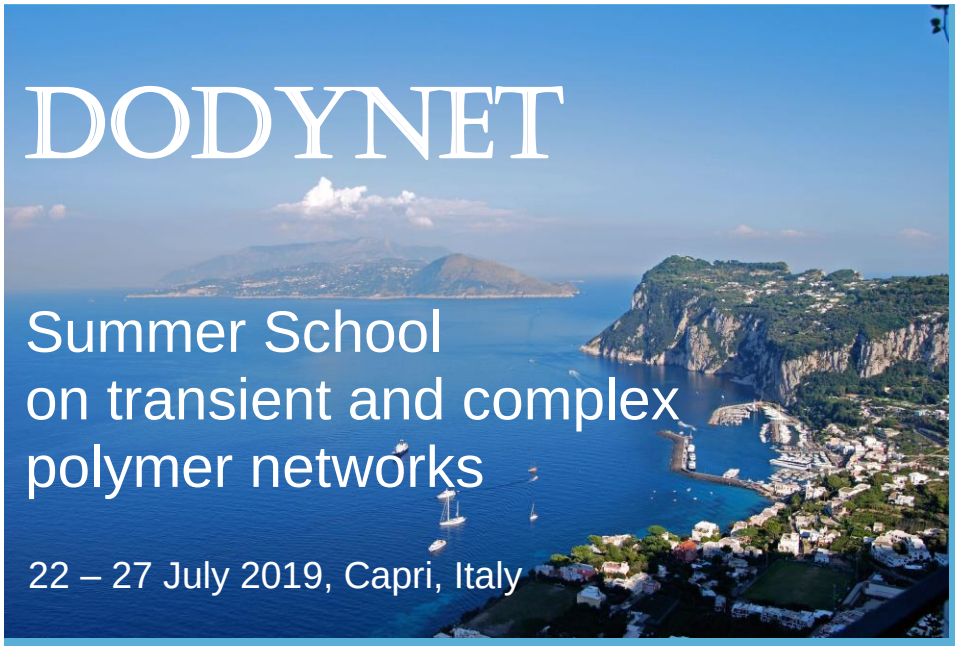
Secondment discussion

The secondments need to be discussed with the students to see if they are relevant and if any students would like to change their secondments. Any information on changes needs to be reported to Christine so the adjustments can be made accordingly.

Questions or suggestions

Students have two questions relayed by their representatives. They would like to have more information on their presentation in DTU for the Mid-Term Check. This information will be given during this meeting. They also ask if they can buy a laptop for their work. Regarding this point, there is no objection from the Project Coordinator but they have to check with the rules of their university.

DODYNET



Summer School on transient and complex polymer networks

22 – 27 July 2019, Capri, Italy

The DoDyNet Supper School will be held from the 22nd to the 27th of July 2019, on the beautiful island of Capri.

The school aims to explore all aspects of polymer networks containing supramolecular junctions or several dynamics of asso

ciation.

The school is addressed to students and researchers both from industry and academic institutions, and is open to all with an interest in this field.

Participants will also have an opportunity to present their own work during poster sessions.

Organisers

The summer school is organized by Prof. Giovanni Ianniruberto, (Dipartimento di Ingegneria chimica, dei Materiali e della Produzione industrial, Università Degli Studi di Napoli Federico II) and Prof. Evelyne van Ruymbeke (Bio- and Soft-Matter, Université catholique de Louvain). This project has received funding from the European Union as an Innovative Training Networks under the H2020 Marie Curie Actions programme.

Confirmed Invited Speakers

- Ralph Colby (Penn State University)
- Salvatore Coppola (Versalis, Italy)
- Emanuela Del Gado (Georgetown University, USA)
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- Yuichi Masubuchi (Nagoya University, Japan)
- Bradley Olson (MIT, USA)
- Daniel Read (University of Leeds, United Kingdom)
- Michael Rubinstein (University of North Carolina, USA)
- Ilja Voets (Eindhoven University of Technology, The Netherlands)
- Zuowei Wang (University of Reading, United Kingdom)
- Hiroshi Watanabe (Kyoto University)

Registration fee

• 300€, this includes all course materials, coffee breaks and lunches, as well as a social dinner
• Note that places are limited, so please register early
• Registration at https://www.dodynet.eu/capri-summer-school-july-

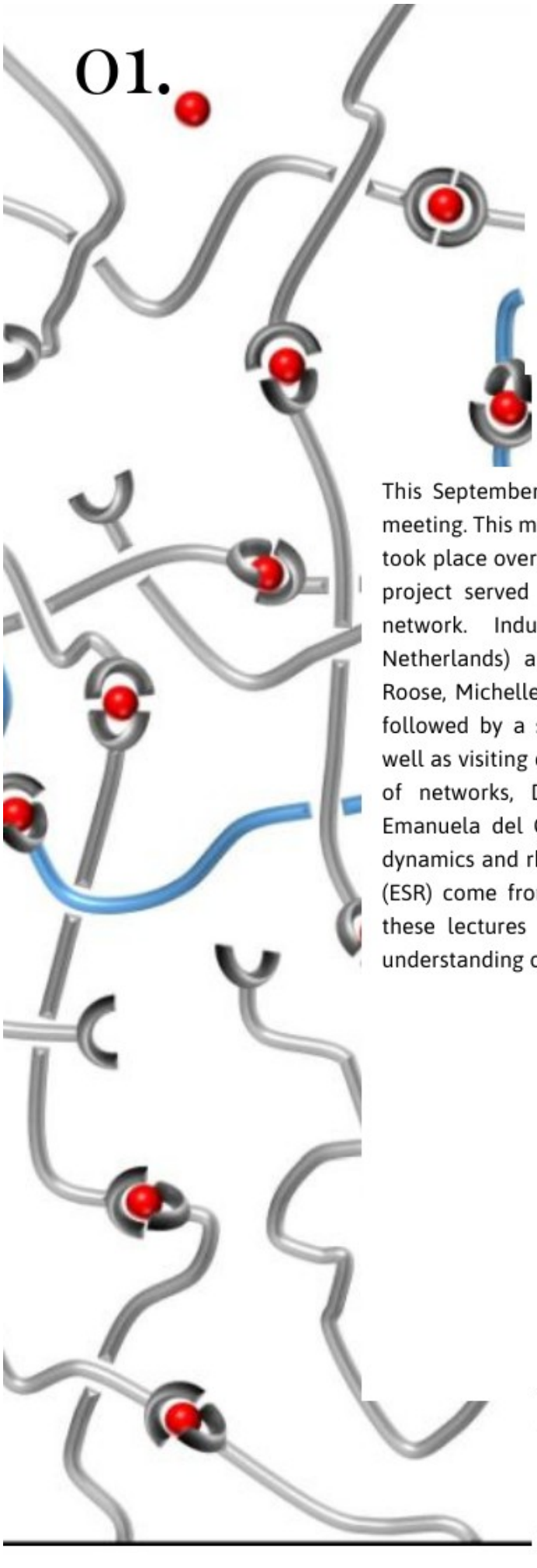
Appendix 11 : Newsletter following the first project meeting in September 2018, FORTH, Heraklion, Crete

Appendix 12 : Newsletter following the second project meeting in January 2019, DSM, Geleen, The Netherlands

Newsletter Intermediate Meeting Heraklion 2018

DoDyNet

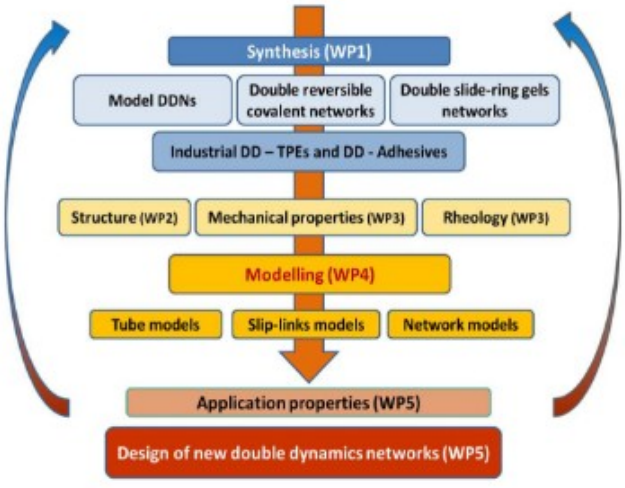
INITIAL TRAINING NETWORK



01.

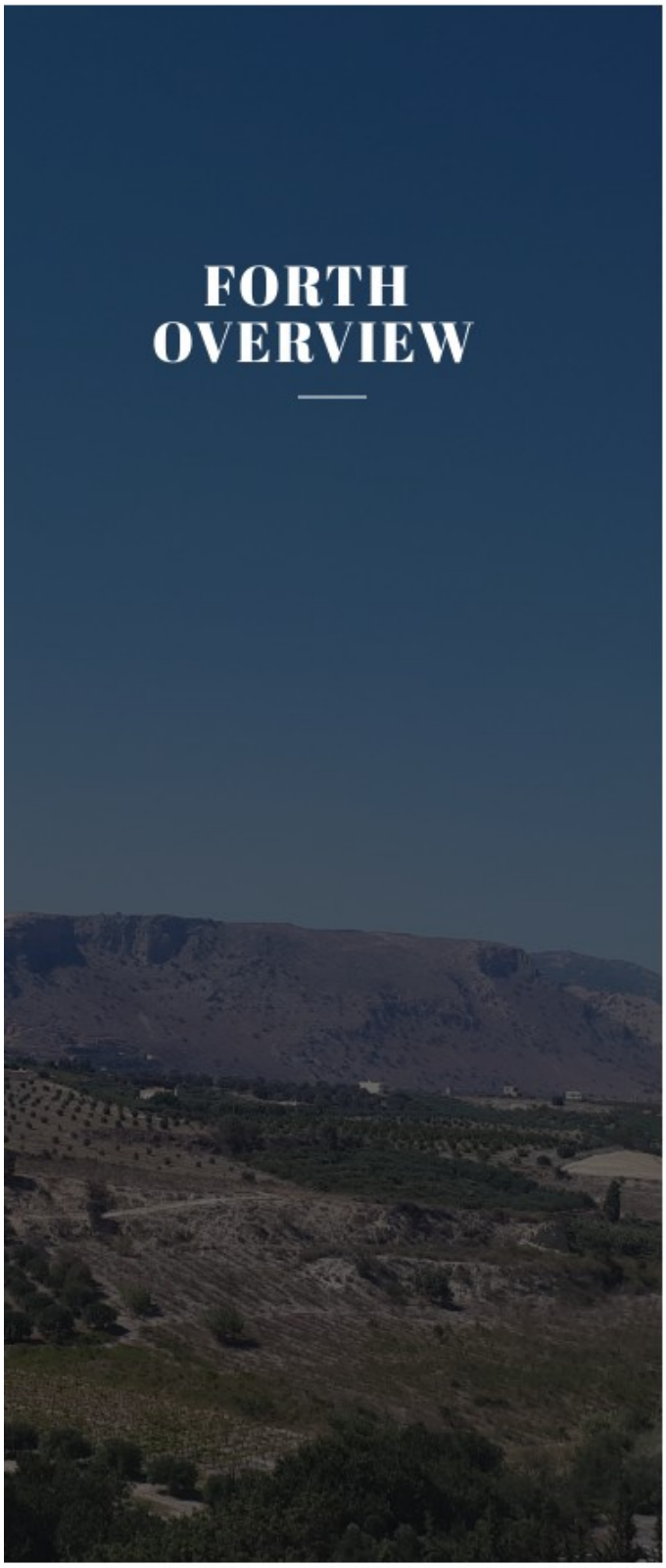
Innovative Training Network (ITN)
Marie-Curie Actions

This September, the DoDyNet group had their first intermediate meeting. This meeting
took place over the course of a week in Heraklion, Greece. First the project served as a way of introducing members to the entire network. Industrial partners Allnex (Belgium), DSM (The Netherlands) and tesa (Germany) were represented by Patrice Roose, Michelle Seitz and Stephan Zoellner respectively. This was followed by a series of lectures from participating professors as well as visiting experts Giuseppe Marucci (UNaples) on generalities of networks, Daniel Reed (ULeeds) on polymer physics and Emanuela del Gado (Georgetown University) on the microscopic dynamics and rheology of soft gels. As the Early Stage Researchers (ESR) come from varying scientific backgrounds, the objective of these lectures was to ensure that everyone starts with a basic understanding of each part of the network.



This is how Dodynet works: Samples synthesised in one work package (WP1) are characterised for structure, rheological and mechanical properties in another (WP2 and WP3) and then modelled (WP4) at the same time with continual feedback between each group to advance the research.

02.



FORTH OVERVIEW

The Foundation for Research and Technology - Hellas (FORTH)

It was established in 1983, is one of the largest research centers in Greece. They are active in fields as varied as electronics, molecular biology and cultural studies and promote scientific progress through collaboration with international partners and high quality research.

The Institute of Electronic Structure and Laser (IESL) was one of the three initial institutes founded in 1983. It has since established its international presence in the areas of Laser Science, Micro/nano-electronics, Polymer Science, Materials Science and Astrophysics.

The Polymer and Colloid Science group focuses on the rheology and dynamics of model polymer and colloidal systems with expertise in scattering techniques (dynamic, neutron, X-ray).

This is the lab where ESR Consiglia Carillo and Christina Pyromali work with Prof. Dimitris Vlassopoulos.

03.

TEAM PRESENTATION

Clément Coutouly

Clément Coutouly
ESR 1, works on the synthesis and
dynamics of model supramolecular polymer networks at Université catholique de Louvain in Belgium under the supervision of Prof. Charles-André Fustin and Prof. Evelyne Van Ruymbeke.

Rowanne Lyons

Rowanne Lyons
ESR 2, works on the synthesis and rheological analysis of double dynamic networks based on slide ring gels at the Université catholique de Louvain in Belgium under the supervision of Prof. Charles-André Fustin and Prof. Evelyne Van Ruymbeke.

Larissa Hammer

ESR 3, works on the design and synthesis of double dynamic networks based on reversible covalent bonds at ESPCI Paris, France under the supervision of Renaud Nicolaÿ.

Stefania Traettino

ESR 4, works on "supramolecular double-networks based on microgels with reversible covalent interactions" at Laboratoire Matière Molle et Chimie, ESPCI Paris, under the supervision of professor Michel Cloitre.

Christina Pyromali

ESR 5, studies the linear and non-
linear viscoelastic response of double dynamics networks under large shear deformation at FORTH, Greece, under the supervision of Dimitris Vlassopoulos.

Wendi Wang

ESR 6, studies viscoelastic response of double dynamics networks under transient elongation at Danmarks Tekniske Universitet (DTU) in Denmark under the supervision of Qian Huang, Ole Hassager and Anne Ladegaard Skov.

Carole-Ann Charles

ESR 7, studies the elastocapillary effects on double dynamics networks at Laboratoires Charles Coulomb in Montpellier, France, under the supervision of Christian Ligoure and Laurence Ramos.

04.

TEAM PRESENTATION

Consiglia Carillo

ESR 8, studies the deformability and fracture mechanisms in reversible covalent DDNs at FORTH in Heraklion under the supervision of Dimitris Vlassopoulos.

Simone Sbrescia

ESR 9, studies the influence of temperature and composition on mechanical properties of DD-Thermoplastic Elastomers at DSM in The Netherlands under the supervision of Michelle Seitz and Tom Engels, officially enrolled at UCL in Louvain-la-Neuve with Evelyne van Ruymbeke as supervisor.

Paola Nicolella

ESR 10, studies the structure and diffusion in DDNs at the nano- to micro- scale at Johannes Gutenberg-University Mainz in Germany (Department of Physical Chemistry) under the supervision of Prof. Dr. Sebastian Seiffert.

Hongwei Liu

ESR 11, studies the nonlinear rheology of reversible double dynamics networks at Università degli Studi di Napoli Federico II in Napoli, Italy, under the supervision of Giovanni Ianniruberto

Yanzhao Li

ESR12, modelling the linear dynamics of double dynamics polymer networks at Université catholique de Louvain in Louvain-la-Neuve, Belgium under the supervision of Evelyne Van Ruymbeke.

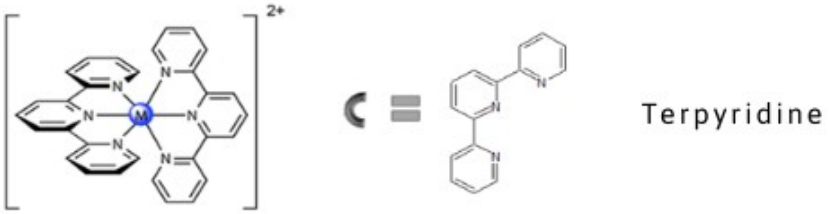
Jianzhu Ju

ESR 13, studies the application property of double dynamics networks at Laboratory of Soft Matter Science and Engineering in ESPCI, Paris, France, supervised by Costantino Creton and Tetsuharu Narita.

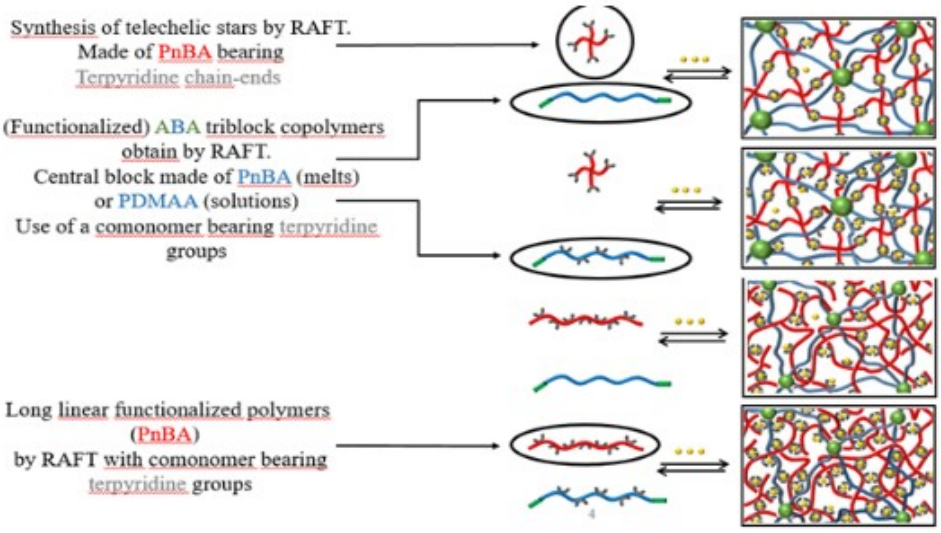
05.

EXPERIMENTS

At this stage, many ESRs are at the beginning of their research. Nevertheless, the earliest researchers recruited, Carole Ann and Clément have already made great progress:
Clément Coutouly, *ESR 1, UCLouvain*, has been working on the synthesis of model double dynamic networks based on metal-ligand interactions. Terpyridine ligands and divalent metal ions form stable complexes:



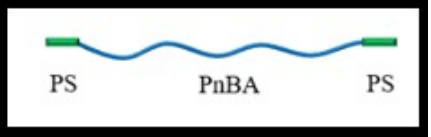
The goal is to develop durable double network gels with strong mechanical properties, which can be achieved in three ways:



The synthesis of long chain ABA triblock copolymers has been achieved with poly n-butylacrylate (PnBA) and polystyrene (PS) in the melt state. The amount of PS was varied from 2-5%, with a turbid aspect observed at 5% PS.

PS 3%

PS 5%

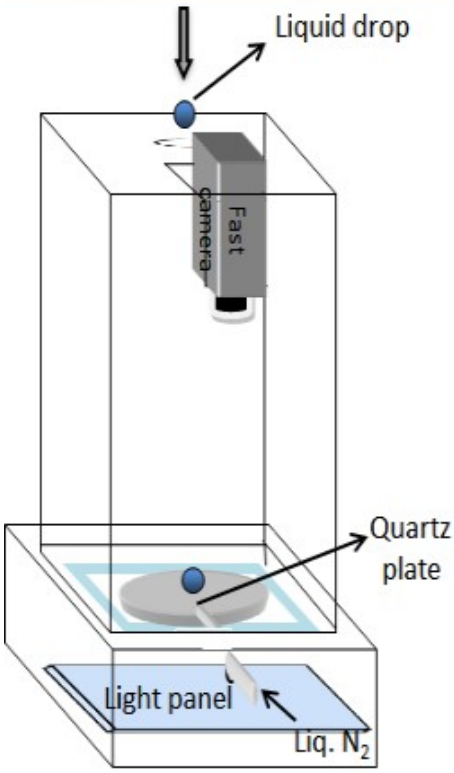


06.

EXPERIMENTS

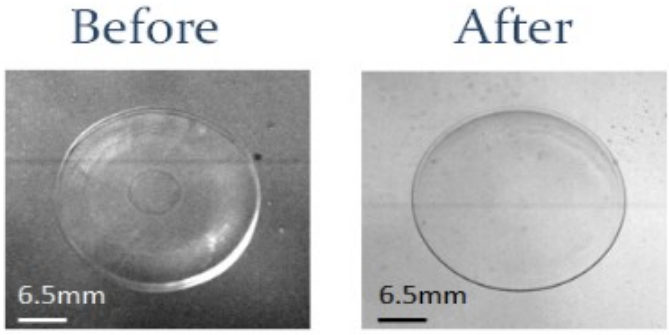
These copolymers were also successfully functionalized with 0.5% of terpyridine.

The next steps include increasing the percentage of terpyridine ligands to 2% and investigating the possible phase separation that may be occurring at higher PS levels. A total of 11 samples were immediately available for Dodynet members. Bravo Clément!

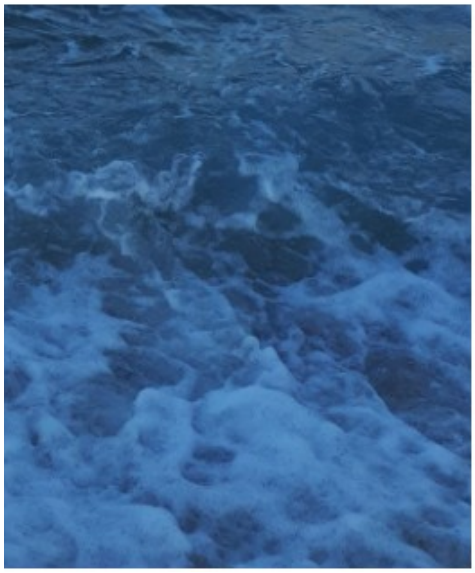


Carole-Ann Charles, ESR 7, Laboratoire Charles Coulomb, has been working on improving and characterizing a setup allowing the study of drop impact dynamic with minimized shear dissipation. This setup uses the inverse of Leidenfrost effect by performing the impact on a thin layer of liquid nitrogen that evaporates when the drop at ambient temperature comes into contact with it, forming a vapor cushion on which the drop can expand radially freed from shear dissipation.

By changing the surface of impact from a silicon wafer to a quartz plate, a semi-automatic analysis of the data is now possible and a study of the sheet thickness field is conceivable thanks to the better contrast.



S. Arora et al., 2017

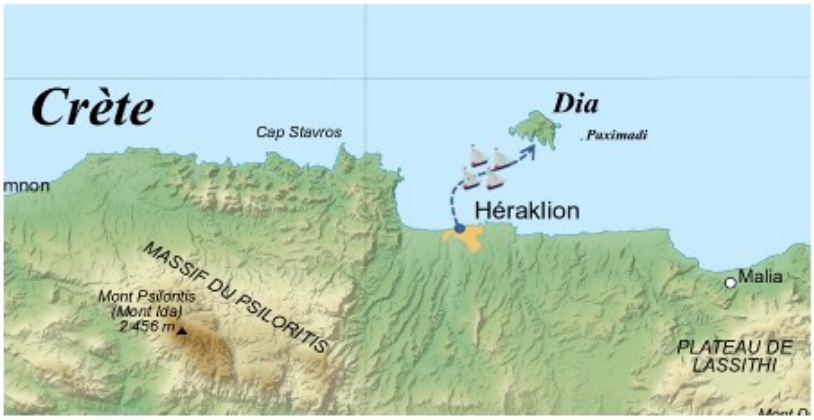


Subsequently this setup will be used to study the impact of double dynamic networks and will allow to rationalize the different roles of inertia, elasticity, capillarity and dissipation.

07.

Dia Excursion

Of course in such a beautiful setting, we did not spend all our time in the laboratory! On Sunday 23rd, we sailed up to Dia, an island 7 miles north of Crete with a rich history.



According to mythology, after the people of Crete angered Zeus, he created a giant sea monster to destroy them but was persuaded to change his mind and he petrified it instead. This might explain why it's still uninhabited...

Both professors and students enjoyed a peaceful day of sunbathing and swimming on this beautiful island without an incident to declare during the outing!

08.

Next Meeting : DSM 2019

As a European Union funded initiative, one of the goals is to maximise collaboration between partner universities and industrial partners. This will be achieved through periodic internships for each ESR as well as regular meetings with all members.

The next meeting will be organized by DSM in the Netherlands from the 29th January – 2nd February 2019.

See you then!

The DoDyNet Summer School
22 - 27 July 2019
Capri

The school is addressed to students and researchers both from industry and academic institutions.

Confirmed invited speakers :

Ralph Colby (Penn State University)
Emanuela Del Gado (Georgetown University, USA)
Jian Ping Gong (Hokkaido University, Japan)
Giuseppe Marrucci (Naples University, Italy)
Daniel Read (University of Leeds, United Kingdom)
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Hiroshi Watanabe (Kyoto University)

The DoDyNet Team

INITIAL TRAINING NETWORK

DODynet

www.dodynet.eu

Newsletter
Annual Meeting I
DSM January 2019

INITIAL TRAINING NETWORK
PODFnet

01.

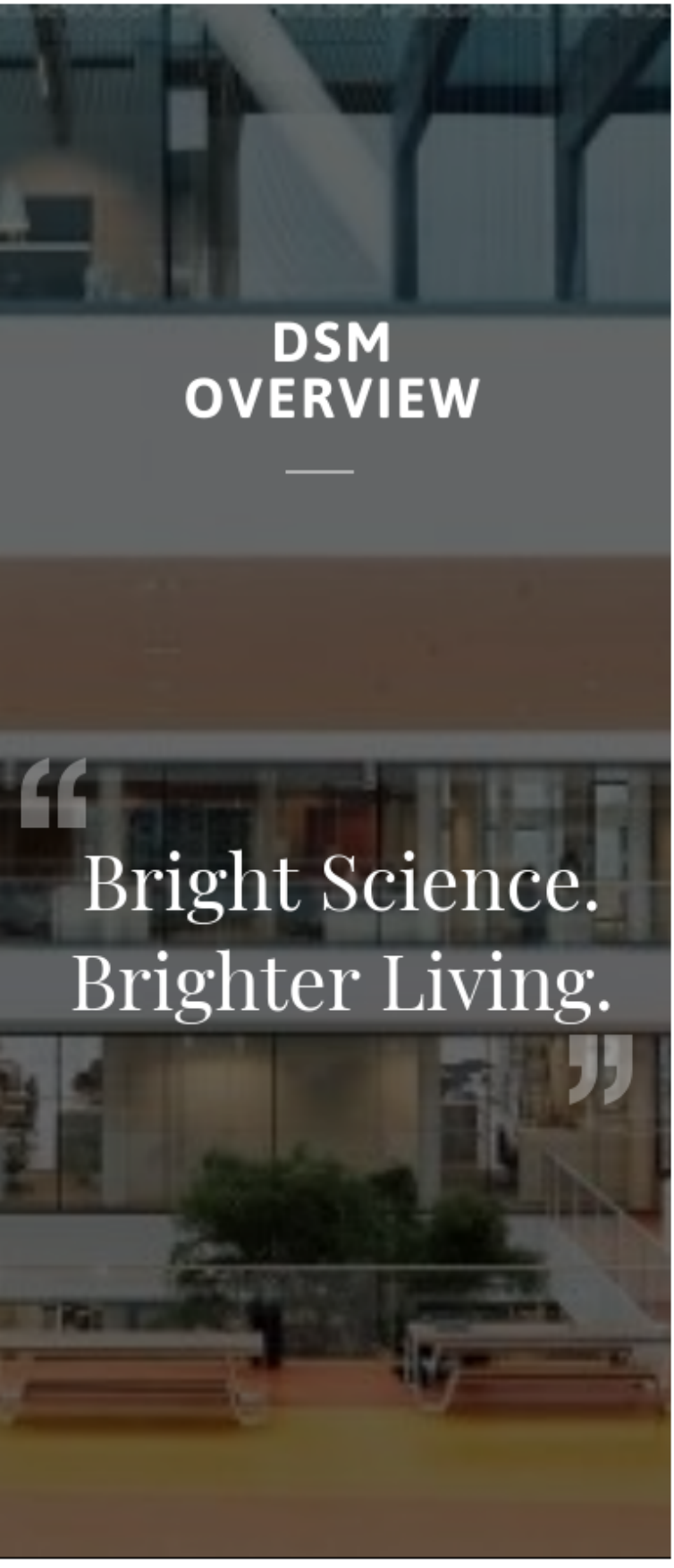
DSM Material Science Center

Geleen, The Netherlands

The first annual meeting took place in January in the Netherlands. The first day was in DSM Material Science Center: the day started with a welcome and introduction of DSM and followed by interesting lectures and debates based mostly on the importance of Safety in a working environment and differences between an industry and academic career, as for example on how to read a patent, the role of a Product Developer and of a Sustainability Engineer.

The lectures were followed by Lab tours: the ESRs were guided through the mechanical lab, where they attended a tensile test executed on different materials and they discussed about the main issues which are possible to face while running such tests. In the rheology lab, all the different equipments for rheological tests were shown. Each test is done to investigate specific material's features under different external conditions. And finally, the students went to the compounding area. They were shown how a material is produced in an industrial scale together with all the possible issues that could arise when working in an environment like that and how to avoid them.

02.



Industry

Royal DSM is a global purpose-led, science-based company in Nutrition, Health and Sustainable Living.

History

DSM and its associated companies deliver annual net sales of about €10 billion with approximately 23,000 employees. The company was founded in 1902 and is listed on Euronext Amsterdam.

Services

Creating better, more sustainable materials
DSM's expertise in Materials Sciences is what helps them produce many of the engineering thermoplastics, resins, high performance fibers and coatings that appear in products essential to everyday lives – from cars to electronics to packaging to construction to sports and medical equipment and the energy sector.

03.

AGENDA

Later in the day the group moved to Vaalsbroek where the intermediate meeting continued over the course of the week. During the first day in Vaals lectures on mechanical tests and fracture mechanics, small and wide angle x-ray techniques and on fatigue and lifetime prediction took place. The following lecturers were given.

Costantino Creton
ESPCI Paris

Introduction to mechanical testing of soft solid polymers
Large strain viscoelasticity in solids, fracture mechanics, elements of adhesion

Julian Oberdisse
Université de Montpellier

Small angle scattering techniques (neutrons and X-rays), examples of structure modification upon deformation

Luigi Balzano
DSM Research

Wide angle X-ray scattering upon deformation : what can we learn ?

Tom Engels
DSM Research

Fatigue and lifetime prediction strategies for polymers

04.

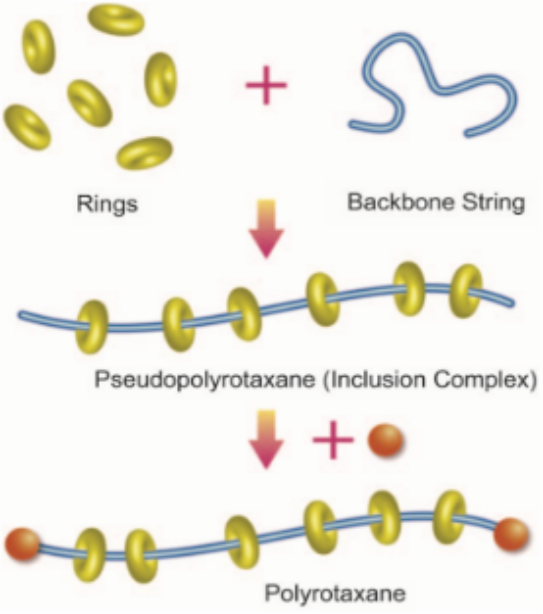
Project Meeting

All ESRs have started their project since a few months now. So for the following two days, ESRs presented the progress they made on their project and their plan for future work.
The first day started by an interesting lecture by Ralph Colby (Penn State University) on the flow induced crystallization of semi-crystalline polymers.

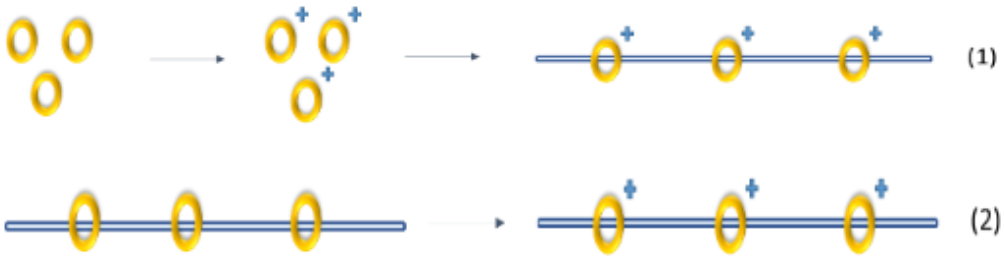
ESR Presentations

ESRs showed quite impressive progress in their work.
The presentations started with the ESRs in charge of the synthesis of DDNs towards the study of their properties and the modeling part.
Here we will present briefly the work of Rowanne, Larissa and Simone.

Rowanne Lyons, ESR 2 UCLouvain, has been working on the synthesis of double dynamics networks based on slide ring gels. Synthesis on the design of these new materials is a two-step synthesis by first adding the rings on backbone String and then add a stopper at the end-chain to keep the slide rings along the backbone.



The main target is to develop functionalized rings. For this objective, two strategies are studied: firstly with pre-functionalization rings (1) and secondly with post-functionalization rings (2).

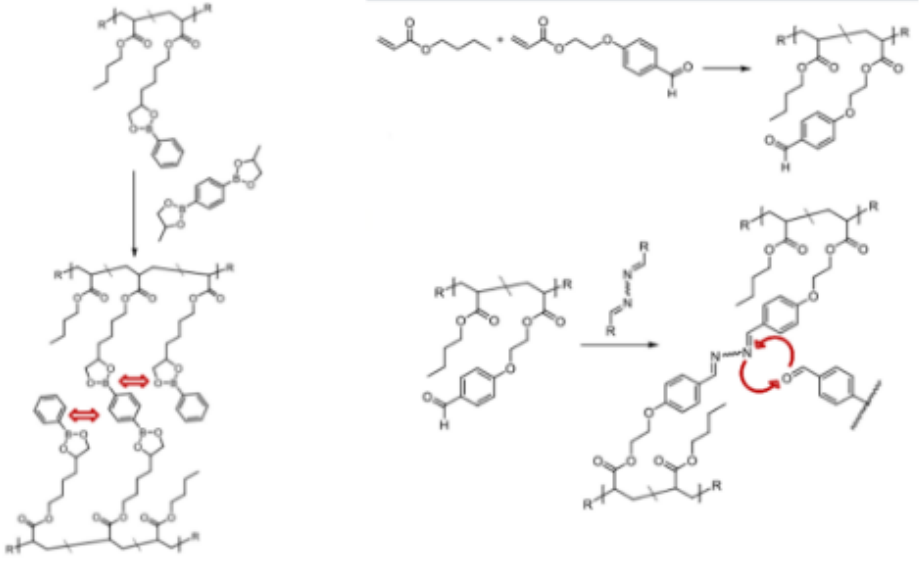


We can already see great improvement in the synthesis and we hope gels will be available soon.

Design and synthesis of double dynamics networks based on reversible covalent bonds

Larissa, ESR 3, ESPCI has been working on the design and synthesis of double dynamics networks based on reversible covalent bonds.
Two systems are currently studied, one based on Boronic ester exchange (3) and the other one, on imine exchange (4).

(3) (4)



So far, Larissa reported impressive results on the improvement of synthesis route to form the first network based on boronic ester exchange. The aim is to develop two interpenetrating networks structures using orthogonal cross-links.

06.

Mechanical tests on soft thermoplastic elastomers

Simone Sbrescia, ESR9, presented the results he obtained in DSM from mechanical tests on soft thermoplastic elastomers developed by DSM itself. He demonstrated the influence that molecular weight and composition can have on the mechanical properties of these materials and how these properties change by increasing temperature. In particular, they show an unexpected embrittlement by increasing temperature, while standard semi-crystalline polymers show the opposite behavior (FIGURE A). Based on these results, to understand the failure mechanism of these materials, it was decided to run fracture tests on these materials to see what happens locally, where the failure starts.

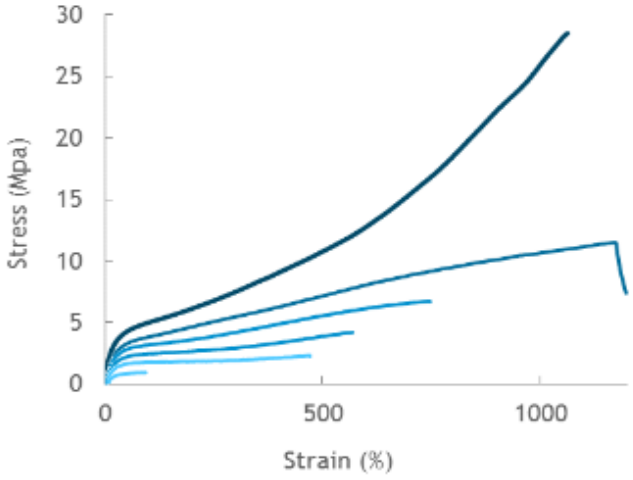


FIGURE A : Engineering stress-strain curves obtained for a soft thermoplastic elastomer at different temperatures. Temperature is increasing from dark to light

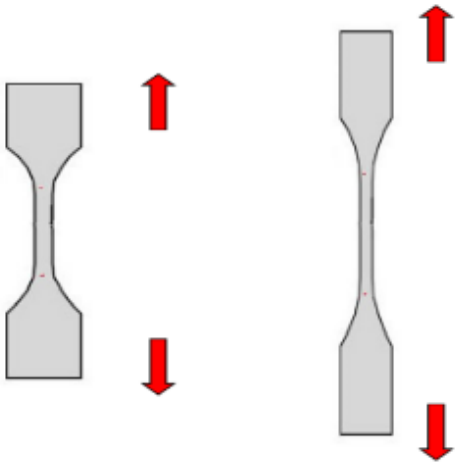


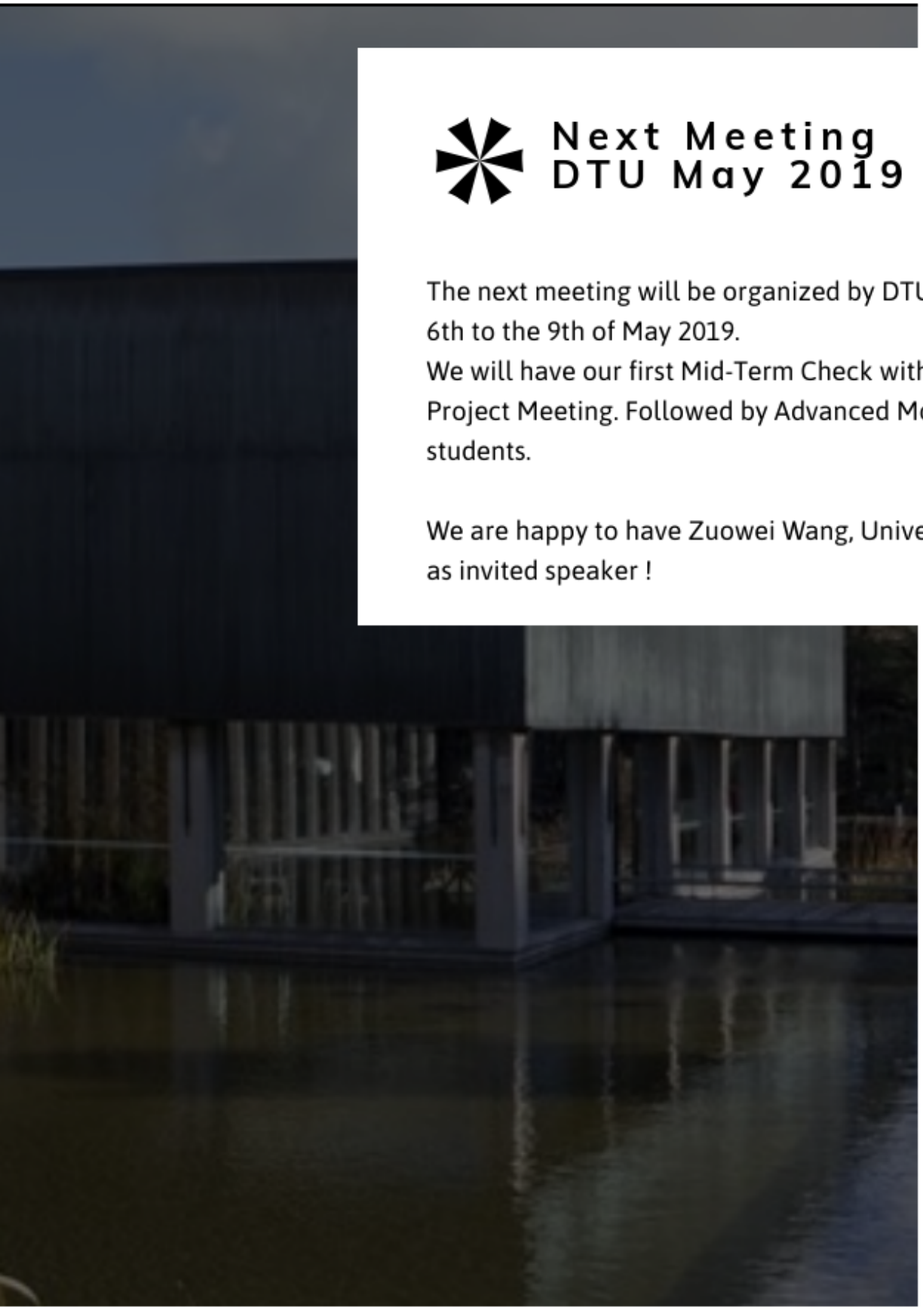
FIGURE B : Typical dog bone shaped specimen used for tensile testing. Displacement is applied along the direction pointed by the arrows. Force and displacement between the two dots are collected leading to the graph of FIGURE A

07.

During the DSM meeting, exchanges between partners universities and industrial partners were fruitful.

For example, Consiglia Carillo, ESR 8 FORTH, is already doing Rheological studies on samples Clément, ESR 1 UCLouvain, provided. Others are working on star polymer and samples agreements have already been done. And of course, tesa, Allnex and DSM are supplying samples for rheological and mechanical studies helping ESRs build a process to further study Double Dynamics Networks.

Our ESR Team at work with Michelle Seitz, DSM



Next Meeting DTU May 2019

The next meeting will be organized by DTU in Denmark from 6th to the 9th of May 2019.
We will have our first Mid-Term Check with our traditional Project Meeting. Followed by Advanced Modules II for our students.

We are happy to have Zuowei Wang, University of Reading, UK as invited speaker !

See you then!

ICR Institute for Chemical Research International Joint Usage/Research Center

DODYnet

DODYNET

Summer School on transient and complex polymer networks

22 – 27 July 2019, Capri, Italy

The DoDyNet Summer School will be held from the 22nd to the 27th of July 2019, on the beautiful island of Capri.

The school aims to explore all aspects of polymer networks containing supramolecular junctions or several dynamics of association.

The school is addressed to students and researchers both from industry and academic institutions, and is open to all with an interest in this field.

Participants will also have an opportunity to present their own work during poster sessions.

Organisers

The summer school is organized by Prof. Giovanni Iannirubertо, (Dipartimento di Ingegneria chimica, dei Materiali e della Produzione industrial, Università Degli Studi di Napoli Federico II) and Prof. Evelyne van Ruymbeke (Bio- and Soft-Matter, Université catholique de Louvain). This project has received funding from the European Union as an Innovative Training Networks under the H2020 Marie Curie Actions programme.

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- Michael Rubinstein (Duke University, USA)
- Ilja Voets (Eindhoven University of Technology, The Netherlands)
- Zuowei Wang (University of Reading, United Kingdom)
- Hiroshi Watanabe (Kyoto University, Japan)

Registration fee

- 300€ this includes all course materials, coffee breaks and lunches, as well as a social dinner
- Note that places are limited to 70 participants, please register early
- Registration at https://www.dodynet.eu/capri-summer-school-july-2019/registration/
- Deadline for registration: 29 April 2019
- Deadline for poster submission: 14 June 2019
- Please book your accommodation as soon as possible – July is peak tourist season on the island
- Contact: iannirub@unina.it or dodynet-manager@uclouvain.be