

DoDyNet - Workpackage 1 – Deliverable 1.17 Number 7 :

Yearly ESR Progress Report

1. ESR Annual Report – Year 1 : ESR 1 Clément Coutouly

- *ESR*

Clément Coutouly, ESR 1, Synthesis and dynamics of model supramolecular polymer network

- *Work summary : period 1/11/2017 → 31/10/2018*

I started my PhD in March 5.

The first duty was to understand the meaning of the project and the role I would play in it. An overview on the double networks and the rheology was needed.

Then, the design of ABA triblocks started as soon as the polymer composition was decided with PnBA as central block and Polystyrene as outer block.

According to the RAFT polymerisation, a CTA agent was selected and synthesized according to literature.

First, kinetics studies have been made to control RAFT polymerisation of Polystyrene and design several Polystyrene with different length, it means with different Molar mass. At this point, the synthesis of different Macro-RAFT agent (polystyrene) with different molar mass was controlled and duplicated.

The second part was to synthesize the central block made of PnBA. At the lab, methods to synthesize long linear PnBA have been developed. These methods have been modified to fit with our targeted molecular mass.

Once ABA triblocks synthesized, some rheology tests in shear have been investigated to understand the influence of the outer blocks, and observe any phase separation which is the main target of these systems.

In parallel, Functionalised ABA triblocks have been developed with the same composition but there is the introduction of terpyridine-nBA monomer along the linear chain (0.5%) to introduction metal-ligands interactions in the system while forming gels.

Currently, one more composition of (functionalized) ABA triblock have been developed and other outer blocks are considered.

Finally, specific solvents for middle bloc and which are non solvent for the outer blocks are investigated to form gels with ABA triblocks. And in the next weeks, metallo-supramolecular gels will be study.

▪ *Deliverable and Milestones*

I am a part of WP 1, synthesis and preparation of new DDNs. Synthesis of model DDNs are divided in four different task:

- Synthesis of telechelic star polymers
- (Functionalized) ABA triblock copolymers
- Long linear functionalized polymers
- Elaboration of DDN and role of their composition

Currently, the synthesis of (Functionalized) ABA triblock copolymers have been developed with different systems:

Name	PnBA Molecular Mass ^a (g/mol))	PDI ^a	Sample Mass (g)
CC-021	93 906	1,18	9

Name	PS Molecular Mass ^a (g/mol)	PnBA Molecular Mass ^a (g/mol))	Composition in PS (%)	PDI ^a	Sample Mass (g)
CC-014	2403	109 235	2,1	1,23	3,4
CC-003	3722	80 362	4,4	1,29	1,2
CC-004	3722	84 806	4,2	1,12	0,5
CC-010	3722	113 565	3,2	1,24	2,4
CC-007	6119	105 779	5,5	1,19	3,5
CC-009	6119	103 939	5,5	1,22	1,1

Name	PS Molecular Mass ^a (g/mol)	PnBA Molecular Mass ^a (g/mol))	Composition in PS (%)	PDI ^a	Sample Mass (g)
CC-028	2394	121 923	1,9	1,24	2,6
CC-027	3560	108 348	3,2	1,25	2,1
CC-029	5386	179 231	2,9	1,4	1,5
CC-032	6371	127 526	4,7	1,24	1,6

▪ *Publications and conferences*

The 28-29 of May, I attended to the annual meeting of Belgian Polymer Group in Blankenberge.

The meeting provided a forum to discuss all current topics in polymer science, both by industrials and academics. The meeting was also a platform for young Belgian polymer scientists to present their work via oral communications and posters. The program has been further strengthened by three invited lectures:

- Prof. Yusuf Yagci (Istanbul Technical University) - BPG 2018 award winner
- Dr Nicolaas-Alexander Gotzen (Robert Bosch N.V.)
- Dr Jérôme Sarrazin (ExxonMobil Chemical Belgium)

▪ *Courses followed*

Here, a list of the courses followed during the project meeting:

- Introduction to Polymer Synthesis (Renaud Nicolaÿ, ESPCI)
- Introduction to supramolecular polymers (Charles-André Fustin, UCLouvain)
- Basic Polymer Science (Daniel Read, ULeeds)
- Curing chemistry of organic coating systems (Patrice Roose, Allnex)
- Introduction to scattering theory (Daniel Read, ULeeds)
- Introduction to Scattering Techniques (Benoit Loppinet, FORTH)
- Basic molecular rheology (linear regime) (Dimitris Vlassopoulos FORTH)
- High shear (Dimitris Vlassopoulos FORTH)
- Introduction to extensional rheology (Qian Huang, DTU)
- Double Dynamic Networks: a review (Evelyne van Ruymbeke, UCL)
- Basic principles of coarse-grained molecular simulations (Giovanni Ianniruberto, UN)
- Microscopic dynamics and rheology of soft gels: computational approaches and connection to experiments (Emanuela Del Gado, Georgetown University)

Moreover, I am currently following a course in UCL with Pr. Evelyne Van Ruymbeke on Rheology (LMECA2141).

- *Exchange visits*

NA

2. ESR Annual Report – Year 1: ESR 2 Rowanne Lyons

- *ESR*

Rowanne Lyons, ESR 2, Synthesis and dynamics of double networks based on slide-ring materials

- *Work summary : period 1/11/2017 → 31/10/2018*

Attended first conference in Heraklion from 21st-26th September 2018

Bibliographic research on slide ring gels, double networks and rheology

Preliminary steps to create polyrotaxanes which will be used in slide ring gels

- *Deliverable and Milestones*

Deliverable Number	Deliverable Title	WP	Lead Beneficiary	Type	Dissemination Level **	Due Date*
D1.2	Synthesis and basic characterization of DD-slide ring gels	1	UCL (ESR 2)	Report	Public	M20

Preliminary steps to create polyrotaxanes for slide ring gels:

- Began synthesis of polyrotaxane based on PEG-35000 and α -cyclodextrin and functionalized with quaternary ammonium groups

▪ *Publications and conferences*

Attended Dodynet conference from the 21st-26th September 2018 in Heraklion, Crete

This was the first conference for the Dodynet network and an opportunity for all members to meet each other and be aware of each other's research. There were also some Elementary Modules which helped give a basic understanding of topics not in my field of research.

▪ *Courses followed*

During the Dodynet conference from the 21st-26th September 2018 in Heraklion, Crete, Elementary Modules I:

- Introduction to Polymer Synthesis
- Introduction to Supramolecular Polymers
- Synthesis and Dynamics of Metallo-Supramolecular Polymeric Assemblies
- Curing Chemistry of Organic Coating Systems
- Introduction to Scattering Theory
- Introduction to Scattering Techniques
- Basic Molecular Rheology
- High Shear
- Introduction to Extensional Rheology
- Double Dynamics: A Review
- Basic Principles of Coarse-Grained Molecular Simulations
- Microscopic Dynamics and Rheology of Soft Gels: Computational Approaches and Connection to Experiments

Université Catholique de Louvain

- LMECA 2141 – Rheology

▪ *Exchange visits*

NA

3. ESR Annual Report – Year 1 : ESR 3 Larissa Hammer

- *ESR*

Larissa Hammer; ESR03; Design and characterization of novel Double Dynamic Networks (DDNs) based on reversible covalent bonds

- *Work summary : period 1/11/2017 → 31/10/2018*

This project has the aim to develop Double Dynamic Networks (DDNs) with at least one reversible covalent mechanism. The goal is to employ dynamic 'vitrimetric' systems in these DDNs for this has not been reported in literature, yet.

The general approach in this project is to synthesize the DDNs via the cross-linking of two different functionalized thermoplastics based on P(nBA). The cross-linking can be conducted in solution, maintaining a homogenous distribution of the two individual thermoplastics. The network formation is obtained by adding a difunctional small molecule to the functionalized thermoplastics. 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 crosslinking has to be very efficient and go to high yields to control the crosslinking 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 a few chemical reactions that fulfill these criteria.

To obtain the desired reversible covalent DDNs certain milestones have to be accomplished. First, several test polymerizations with nBA have to be conducted to determine the best polymerization conditions. This includes target molecular weight, temperature, solvent, initiator and monomer concentration. The next step is to synthesize the respective monomers and building blocks for the Networks 1 and 2. Subsequently, these building blocks have to be copolymerized with nBA. The thereby synthesized functional thermoplastics are to be analyzed. In the next step, the cross-linking reaction is tested by cross-linking the thermoplastics individually in solution and if this works fine, the thermoplastics of Network 1 and Network 2 are cross-linked simultaneously to create a double network.

The first network (Network 1) is brittle, tightly cross-linked and the minority network. It has a significantly lower molecular weight than the second network (Network 2). The aimed number average molecular weight (M_n) for the thermoplastics forming this network is around 100 000 Da. The functionalization density is 100 crosslinking points per chain, which translates into 10% functionality. Network 1 is sacrificial, the crosslinks have to participate in fast exchange

reactions to dissipate the energy and to undergo self-healing. The boronic ester/diol exchange is a very fast dynamic reaction leading to reversible covalent bonds. The reaction can take place either between a boronic ester and a diol (transesterification) or two boronic esters (metathesis). The first reaction is very fast; the second one is tunable in its reactivity. 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. The DDNs should be readily applicable at room temperature. Therefore, the glass transition temperature (T_g) of the employed polymers has to be significantly below room temperature. The acrylic 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 $(C_7H_{12}O_2)_n$ and a T_g of -49°C . The general plan for the synthesis of Network 1 is to first synthesize a diol functionalized thermoplastics based on a nBA backbone and then crosslink it (simultaneously with and orthogonally to Network 2) with a diboronic ester. The amount of added ester determines the dynamic of the system. The more free diol there is left in the network (respectively the less boronic ester groups are added) the more dynamic is the system. If all free diols react with the boronic esters the system is hardly dynamic.

To achieve the targeted size of the polymer and to determine the right reaction conditions, homopolymerizations with nBA were conducted. The reaction conditions could be set quite well to achieve a polymer of around $M_n = 100\,000$ Da via FRP. After the reaction parameters of the polymerization were set, the synthesis of the building blocks of the copolymer was started. An acetal protected acrylic monomer was synthesized (Figure 1) and subsequently copolymerized with nBA to achieve a copolymer with about 10% functionality (Figure 2).

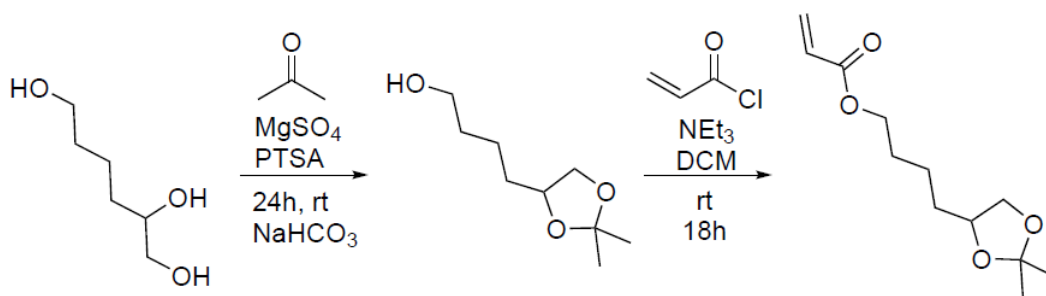


Figure 1: Synthesis of an acetal protected monomer.

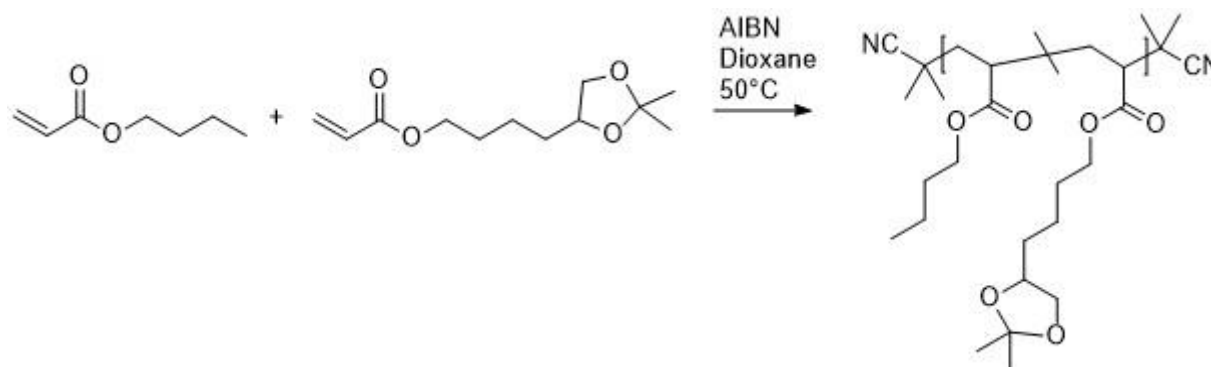


Figure 2: Copolymerization of the acetal protected monomer with nBA.

The next steps for Network 1 are the deprotection of the diol and the crosslinking with a boronic ester.

The second network (Network 2) is the majority network, it 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 T_g . The aimed M_n for the thermoplastics of Network 2 should be around 500 000 Da. The functionalization density aims for 10 crosslinking points per chain, which translates into 0.2% functionality. This network is highly extendable. It is not sacrificial, there should be no bond rupture during expansion. In conclusion, the crosslinks forming this network can be permanent. Yet, the employment of dynamic bonds in this network as well might lead to interesting new properties like advanced self-healing or improved fatigue resistance. However, it has to be taken in account that a more dynamic system might lead to enhanced creep.

As for the non-dynamic systems that can be employed in Network 2 there are several possibilities. As already mentioned above the cross-linking reaction has to be very efficient and strictly orthogonal to the system employed in Network 1. A system that fulfills these criteria is a thiol-ene reaction. It takes place between a thiol and an alkene to form an alkyl sulfide. The reaction is very efficient regarding its high yield, stereoselectivity, high rate, and thermodynamic driving force and is therefore rated as a so called “click reaction”. To use this reaction as crosslinking mechanism, an alkene functionalized has to be synthesized and then cross-linked by a dithiol.

A second alternative would be the crosslinking via an epoxy ring opening. Epoxy rings can be opened very easily by nucleophiles due to the strain of the 3 membered ring. To keep this reaction orthogonal to the Network 1 formation the ring opening is achieved by employing secondary amines as nucleophiles. Here an epoxy functionalized thermoplastic is polymerized

and subsequently cross-linked via the secondary amine. Next to these two permanent crosslinking methods, a third alternative could be employed, creating a network using dynamic crosslinks. 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 either with aldehydes or with other imines, catalyzed by aldehydes (metathesis). So an aldehyde functionalized thermoplastic can easily be cross-linked by a diimine. The amount of still free aldehyde in the network determines the dynamic of the system.

Also for the second network the polymerization conditions were evaluated by homopolymerizations of nBA. However, it was not possible to achieve a polymer with 500 kDa by free radical polymerization. Although, the monomer concentration was increased the molecular weight did not rise above 380 kDa. Depending on the nature of the co-monomer in future experiments alternatives like ATRP or RAFT polymerization could be attempted, if a polymer with a higher molecular weight is demanded.

Simultaneously, the building blocks for the thermoplastics were synthesized. Figure 3 shows the synthesis of the epoxy functionalized acrylic monomer. Figure 4 shows the route to the aldehyde functionalized acrylic monomer.

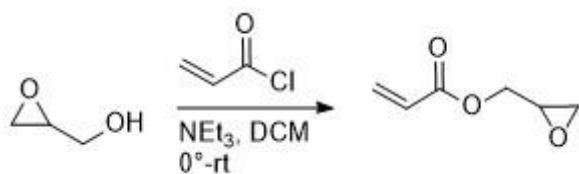


Figure 3: Epoxy functionalized acrylic monomer.

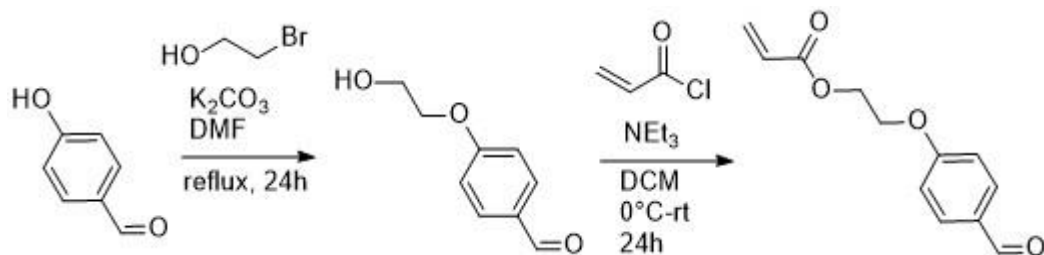


Figure 4: Aldehyde functionalized acrylic monomer.

The thiol-ene system was not approached, yet. The next step for Network 2 is to copolymerize these building blocks with nBA and test the crosslinking reactions.

- *Deliverable and Milestones*

Milestones:

- M1.5 Synthesis and distribution of the first reversible covalent DDNs (Summer 2019)

The concepts of several reversible covalent DDNs have been formed and the synthesis of the building blocks has already started. First thermoplastic precursors have been synthesized and analyzed.

- M1.7 Synthesis and distribution of new reversible covalent DDNs (End of 2019)

Deliverables:

- D1.3 Synthesis and basic characterization of reversible covalent DDNs (Summer 2019)

The concepts of several reversible covalent DDNs have been formed and the synthesis of the building blocks has already started. First thermoplastic precursors have been synthesized and analyzed.

- D2.3 Study structure and homogeneity of reversible covalent DDNs with ESR 10 (Summer 2020)
- D4.3 Relating statistical composition and properties for reversible covalent DDNs with ESR 15 (Spring 2021)
- D5.3 Mechanical behavior of reversible covalent DDNs and link to potential for new applications (Summer 2021)

- *Publications and conferences*

I attended the DoDyNet meeting in Heraklion from the 21.-26.09.2018.

- *Courses followed*

During the DoDyNet meeting in Heraklion I attended the following Elementary Training Modules:

- Introduction to Polymer Synthesis (Renaud Nicolaÿ, ESPCI)
- Introduction to supramolecular polymers (Charles-André Fustin, UCLouvain)

- Curing chemistry of organic coating systems (Patrice Roose, Allnex)
- Introduction to scattering theory (Daniel Read, ULeeds)
- Introduction to Scattering Techniques (Benoit Loppinet, FORTH)
- Basic molecular rheology (linear regime) (Dimitris Vlassopoulos FORTH)
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- Double Dynamic Networks: a review (Evelyne van Ruymbeke, UCLouvain)
- Basic principles of coarse-grained molecular simulations (Giovanni Ianniruberto, UN)
- Microscopic dynamics and rheology of soft gels: computational approaches and connection to experiments (Emanuela Del Gado, Georgetown University)

In addition to that I visit a general French course 6 h a week in the evening. The course includes language lessons to improve my French (grammar, conjugation, spelling, vocabulary, approach to literary texts, and written and oral expression).

- *Exchange visits*

None

4. ESR Annual Report – Year 1: ESR 4 Stefania Traettino

- *ESR*

Traettino Stefania, ESR 4, Supramolecular double-networks based on microgels with reversible covalent interactions.

- *Work summary : period 1/11/2017 → 31/10/2018*

State of art and bibliography concerning microgels, colloidal particles, jammed suspensions of microgels, double networks and rheological studies.

Introduction to the use of different laboratory instruments, paying close attention to the rheometer.

Introduction to different types of microgel (already used by other members of my research group) and how to get them.

Preparation of different microgels that were used as samples for my rheology training.

Analysis of the results obtained from rheological studies on microgels: shear stress, storage and loss modulus.

▪ *Deliverable and Milestones*

No deliverable and milestones during the period covered.

▪ *Publications and conferences*

- “Dodynet Intermediate meeting I” attendance (21st-26th of September 2018, FORTH, Greece).
- Workshop attendance on “Correlated disorder and hyperuniformity in soft matter and photonics” (15-17 October 2018, Institut Henri-Poincaré, Paris).

▪ *Courses followed*

- Introduction to polymer synthesis (Renaud Nicolay, ESPCI)
- Introduction to supramolecular polymers (Charles-André Fustin, UCLouvain)
- Synthesis and dynamics of metallo-supramolecular polymeric assemblies (Flanco Zhuge, UCLouvain)
- Curing chemistry of organic coating systems (Patrice Roose, Allnex)
- Introduction to scattering theory (Daniel Read, ULeeds)
- Introduction to scattering techniques (Benoit Loppinet, FORTH)
- High shear (Dimitris Vlassopoulos, FORTH)
- Introduction to extensional rheology (Qian Huang, DTU)

- Double Dynamic Networks: a review (Evelyn van Ruymbeke, UCLouvain)
- Basic principles of coarse-grained molecular simulations (Giovanni Ianniruberto, UN)
- Microscopic dynamics and rheology of soft gels: computational approaches and connection to experiments (Emanuela Del Gado, Georgetown University)

▪ Exchange visits

Visit to the laboratories of **Foundation for Research & Technology – Hellas (FORTH)** in Greece.

5. ESR Annual Report – Year 1 : ESR 5 Christina Pyromali

▪ ESR

Christina Pyromali, ESR #5, Linear and non-linear viscoelastic response of double dynamics polymer networks under large shear deformation.

▪ Work summary: period 1/11/2017 → 31/10/2018

The last period my research has focused on the following two topics:

1. Rheology measurement techniques

The first division of the research is related to deep understanding of the theoretical background and the hand-on expertise on Rheology Measurement Techniques. More specifically, the first period of the research is devoted to acquiring a strong expertise on how to test the linear and nonlinear shear as well as the linear creep behavior of either entangled and unentangled polymeric materials.

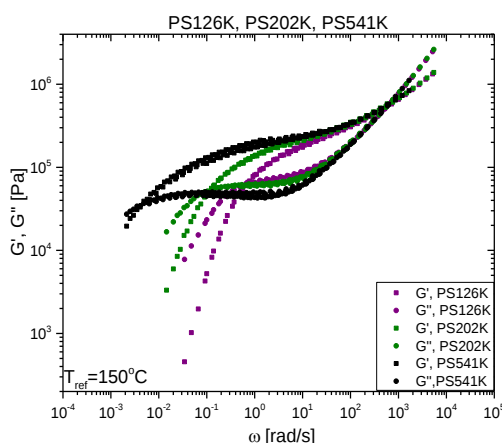


Figure 1: Linear viscoelastic spectra of different molecular weight, entangled Polystyrenes.

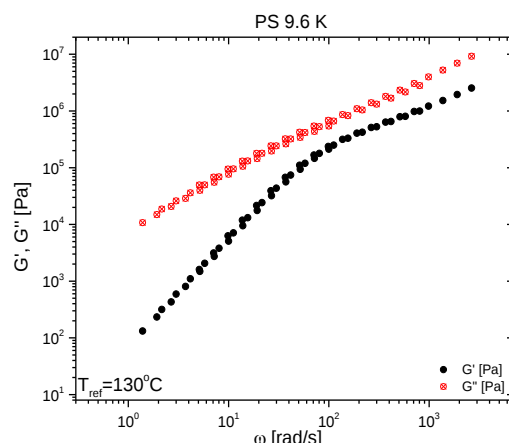


Figure 2: Linear viscoelastic spectra of low molecular weight unentangled Polystyrene.

State-of-the-art, home-made instruments and setups, such as cone and partitioned plate, have been used for characterization of polymer melts with the same chemistry but different molecular weights and number of entanglements. Finally, the results were evaluated for their reliability either theoretically and computationally, using suitable theories (e.g. Tube model, Constraint release, and Contour length fluctuations) and models (e.g. RepTate, NLReg).

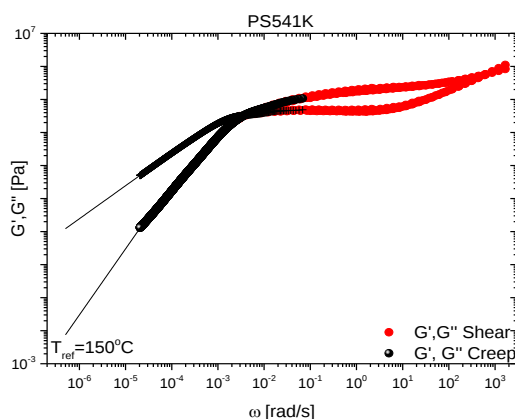


Figure 3: Linear viscoelastic spectra of high molecular weight Polystyrene. The spectra has been extended in the low frequencies converting the linear creep experiments

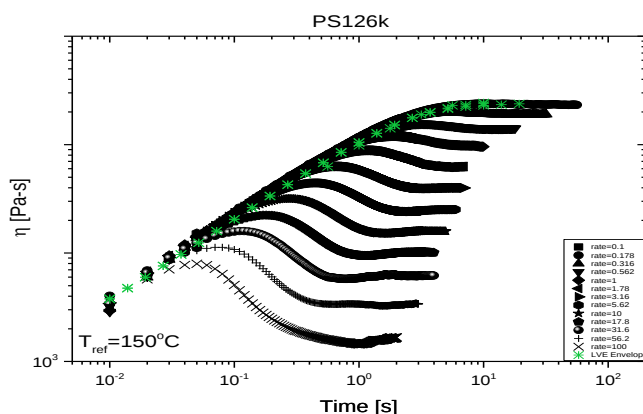


Figure 4: The transient viscosity over time together with the linear viscoelastic envelope.

2. Metal-ligand associated polymer network

Recently, the research interest is focused on the nonlinear shear behavior of entangled, metal-ligand associated polymer networks which is also building block in Double Dynamic Networks (DDNs). This network 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. This transient network has been investigated already it is shown that the relaxation mechanism of such a network depends on both disentanglement and the metal-ligand association dynamics. Also, it is interesting that the stresses are not completely released when the deformation is removed. So, the questions that are mainly addressed relating to the structural evolution during and after nonlinear deformation and the role of the stickers on that. Thus, the protocols have been developed already and the rheological measurements are about to start.

▪ *Deliverable and Milestones*

- Nonlinear shear behavior of model DDNs
- Relating shear thickening behavior and properties of DDNs
- Relating structure and possible inhomogeneities to nonlinear behavior in model DDNs
- Relating creep behavior to adhesive properties

▪ *Publications and conferences*

N/A-TBA

▪ *Courses followed*

- *“Generalities on networks”, Prof Giuseppe Marrucci*
- *Introduction to Polymer Synthesis (Prof. Renaud Nicolaÿ)*
- *Introduction to supramolecular polymers (Prof. Charles-André Fustin)*
- *Curing chemistry of organic coating systems (Dr. Patrice Roose, Allnex)*
- *Introduction to scattering theory (Prof. Daniel Read)*
- *Introduction to Scattering Techniques (Dr. Benoit Loppinet)*
- *Basic molecular rheology (linear regime) (Prof. Dimitris Vlassopoulos)*
- *High shear rheology (Prof. Dimitris Vlassopoulos)*
- *Introduction to extensional rheology (Dr. Qian Huang)*
- *Double Dynamic Networks: a review (Prof. Evelyne van Ruymbeke)*
- *Basic principles of coarse-grained molecular simulations (Prof. Giovanni Ianniruberto)*
- *Microscopic dynamics and rheology of soft gels: computational approaches and connection to experiments (Prof. Emanuela Del Gado)*

- *Exchange visits*

Visiting Experts

- **Seminars, FORTH, Heraklion**

Prof. Michael Rubinstein "Double-Semi dilute Coacervates formed by Oppositely Charged Polyelectrolytes"

Prof. Ralph H. Colby "Shear-Induced Conformational Changes of Flexible and Semi-Rigid Engineering Thermoplastics and their influence on Crystallization"

6. ESR Annual Report – Year 1: ESR 6 Wendi Wang

- *ESR*

Wendi Wang

ESR 6: Viscoelastic response of double dynamics polymer networks under transient elongation

- *Work summary : period 1/11/2017 → 31/10/2018 (PhD started 1/6/2018)*

Introduction

Polystyrene (PS) is a hard and brittle material at room temperature, with glass transition temperature (T_g) around 100°C. It may become flexible when compressed at room temperature in a two-roll milling process (known as "mechanical rejuvenation"). However, this flexibility is temporary. Recently Huang et al. has found that flexible polystyrenes can be obtained by stretching polystyrene melts at a rate faster than the inverse rouse time, followed by rapid quenching below T_g . The resulting samples remain flexible after half a year. This characteristic makes polystyrene a good candidate for optical fibers. However, cracks have been observed while trying to recover the bended sample as shown in Figure 1. The idea of this project is to add some hydrogen bonding between polystyrene molecules so that the cracks at large deformation can be prevented. The resulting system is actually a double network formed by entanglements and hydrogen bonding.



Figure 1: flexible polystyrene (left) and cracks when trying to recover the sample (right)

Experiments

Two different samples have been selected for this project: a pure polystyrene with T_g around 100°C and a polystyrene containing 5% acid group on the polymer chains with T_g around 114°C . These acid groups tend to form hydrogen bonding at room temperature.

The linear viscoelastic properties of these two samples were obtained from small amplitude oscillatory shear measurements. An 8 mm plate-plate geometry was used on an ARES-G2 rheometer from TA Instruments. The non-linear extensional behaviors have been studied above T_g in controlled uniaxial extension using a filament stretching rheometer (Figure 2), where both normal force and diameter evolution were measured. Furthermore, tensile tests and 3-point bending tests were carried out on VADER and RSA3 Dynamic Mechanical Analyzer from TA Instruments respectively.

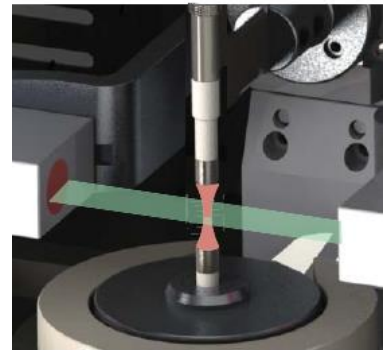
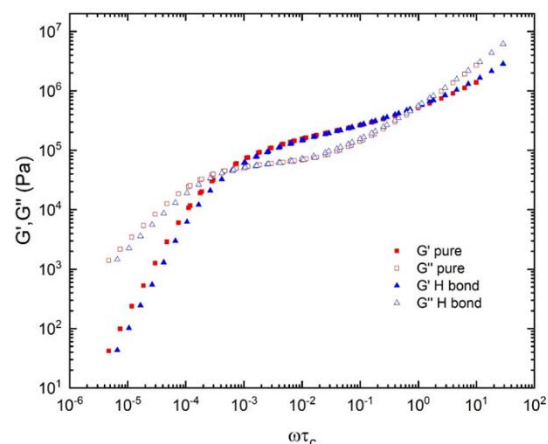
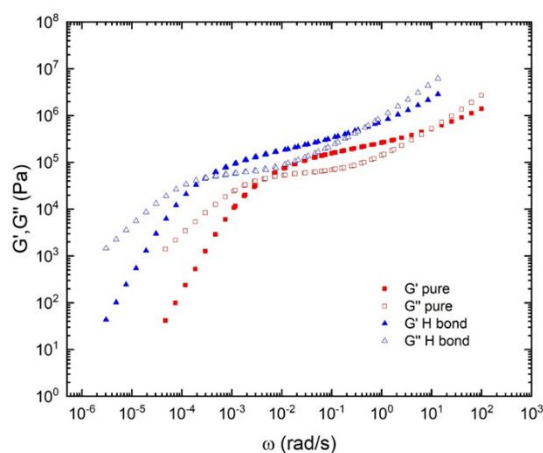


Figure 2: Filament Stretching Rheometer (VADER)

Results and discussions

The linear viscoelastic (LVE) properties of these two samples have been tested at three different temperatures above T_g to build up the master curve, as shown in Figure 3 (a). To compare these



two samples, the frequency on the x-axis is normalized by the second crossover frequency for each sample, as displayed in Figure 3 (b). The two curves overlap each other quite well, indicating a similar number of entanglements per chain for the two samples. It also suggests that the acid groups do not form hydrogen bonding at 130°C.

Figure 3: (a) LVE data at 130°C, (b) LVE data with normalized frequency at 130°C

The non-linear extensional behaviors have been tested at different stretching rate and compared in Figure 4 after normalization. These two samples show similar extensional behavior at high temperature above T_g .

Now we wonder if these two samples still have similar mechanical behaviors at room temperature. Both samples have been stretched faster than inverse Rouse time and quenched fast until room temperature. Then tensile tests have been performed with a constant rate 0.001 s^{-1} at room temperature (blue and red curves in Figure 5). At meantime, full-relaxed samples have also been quenched and tested (black and grey curves). Both two full-relaxed samples are brittle while the other two are flexible. However, the strain softening, which is observed in the blue curve for the pure polystyrene sample, seems to be totally removed in the red curve for the sample with hydrogen bonding. This phenomenon could be explained by enhanced network contribution according to Haward and Thackray model.

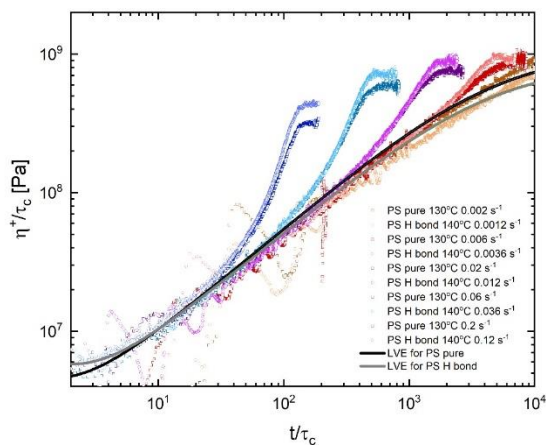


Figure 4: Comparison of normalized extensional stress growth coefficient for two PS sample

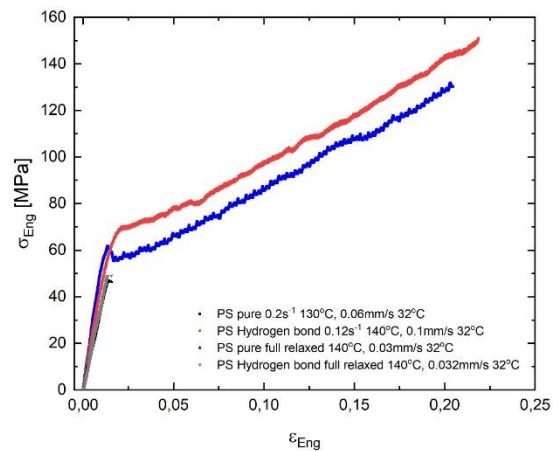


Figure 5: Engineering stress as a function of strain in tensile tests

Future work

The repeatability of experiments should be examined. Furthermore, it is interesting to test the effect of hydrogen bonding in bending tests and depending on the results, a polystyrene containing higher acid group proportion will be studied.

Reference:

- [1] Q. Huang et al., *ACS Macro Lett.* 2018, 7, 1126–1130
- [2] H. E. H. Meijer, *Prog. Polym. Sci.* 2005, 30, 915–938

▪ *Deliverable and Milestones*

Expected date	Deliverables
Oct. 2019	Study of nonlinear extension behavior of model DDNs
Feb. 2020	Study of material parameters and extensibility of new DDNs
May 2020	Study of extensibility and elasticity of DD-slide ring gels
Aug. 2020	Extracting main parameters in DDNs for governing their rheology
Dec. 2020	Relating extensional behavior and their mechanical properties; Understand influence of chain stretching on the lifetime of reversible bonds
Feb. 2021	Relating elongation behavior to adhesive properties

▪ *Publications and conferences*

Have not written publications nor attended conferences yet.

▪ *Courses followed*

PhD students at DTU must follow courses to an extent corresponding to 30 ECTS-points (1 ECTS-point corresponds to about 28 working hours).

Completed course *Rheology of complex fluids* at DTU, 7.5ECTs, August 2018

Following course *Advances in Chemical and Biochemical Engineering* at DTU, 2.5 ECTs, October 2018-present

Followed DoDyNet Elementary Modules I in Crete, September 2018

▪ *Exchange visits*

In DoDyNet network:

Laboratory visit in FORTH during DoDyNet Intermediate meeting I, September 2018

Other visits related to DoDyNet subject:

Visiting professor D. Vlassopoulos (from FORTH, Greece) at DTU during June 2018

Visiting postdoc E. Moghimi (from FORTH, Greece) at DTU in October (one week) 2018

Visiting professor Jinxiong Zhou (from Xi'an Jiaotong University, China) at DTU in October (one week) 2018

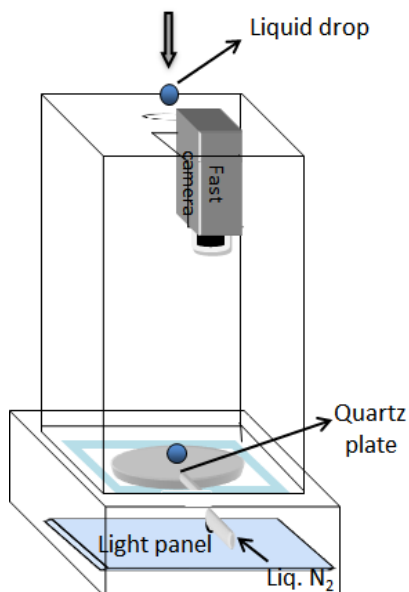
7. ESR Annual Report – Year 1: ESR 7 Carole-Ann Charles

▪ *ESR*

Carole-Ann Charles ESR7 Elastocapillary effects in double dynamic networks.

▪ *Work summary: period 1/11/2017 → 31/10/2018*

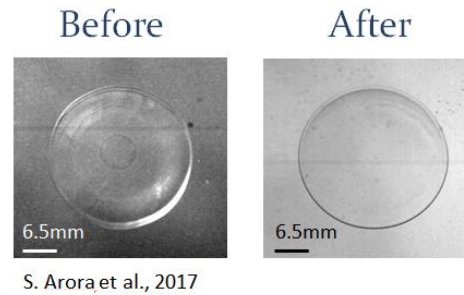
I have been working on improving and characterizing a setup allowing the study of drop impact dynamic with minimized shear dissipation. This setup uses the inverse of Leidenfrost effect by performing the impact on a thin layer of liquid nitrogen that evaporates when the drop at ambient temperature comes 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.

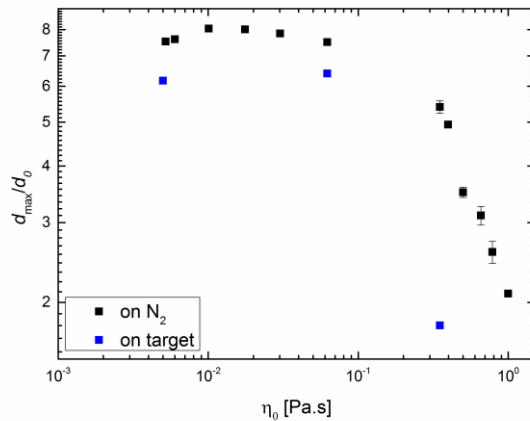
Subsequently this setup will be used to impact of double dynamic networks and to rationalize the different roles of inertia,



study the
will allow
elasticity,
capillarity
and

dissipation.

But for now, it was tested with silicone oils 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 is to use this setup with microemulsions reversibly linked by telechelic polymers. These microemulsions will be colored with water soluble nigrosine and the sheet thickness field will be analyzed using Beer-Lambert law.

▪ Deliverable and Milestones

Deliverable number	Deliverable Title	Work Package	Lead Beneficiary Short Name	Type	Dissemination Level*	Due Date
D3.7a	Elasto-capillarity in DDNs	3	CNRS (ESR7)	Report	PU	M36
D3.7b	Relating Elasto-capillarity and shear	3	FORTH (ESR7)	Report	PU	M40

	properties of DDNs					
D5.7a	Relating Elasto-capillarity and adhesive properties of DDNs	5	ESPIC (ESR7)	Report	PU	M42
D5.7b	Percolation mechanisms in DD-TPEs	5	DSM (ESR 7)	Report	CO	M48

- *Publications and conferences*

NA

- *Courses followed*

Course on the basics of ImageJ software (Biocampus Montpellier) 21h

“Generalities on networks”, Giuseppe Marrucci (UNaples) 45min

Introduction to Polymer Synthesis (Renaud Nicolaÿ, ESPCI) 2h

Introduction to supramolecular polymers (Charles-André Fustin, UCLouvain) 1h 30 min

Basic Polymer Science (Daniel Read, ULeeds) 45min

Curing chemistry of organic coating systems (Patrice Roose, Allnex) 1h 50 min

Introduction to scattering theory (Daniel Read, ULeeds) 1h 30min

Introduction to Scattering Techniques (Benoit Loppinet, FORTH) 1h 30min

Basic molecular rheology (linear regime) (Dimitris Vlassopoulos FORTH) 1h30min

High shear (Dimitris Vlassopoulos FORTH) 1h

Introduction to extensional rheology (Qian Huang, DTU) 1h 30min

Double Dynamic Networks: a review (Evelyne van Ruymbeke, UCL) 1h

Basic principles of coarse-grained molecular simulations (Giovanni Ianniruberto, UN) 1h 30min

Microscopic dynamics and rheology of soft gels: computational approaches and connection to experiments (Emanuela Del Gado, Georgetown University) 2h

- *Exchange visits*

NA.

8. ESR Annual Report – Year 1: ESR 8 Consiglia Carillo

- *ESR*

Consiglia Carillo, ESR8

Deformability and fracture mechanisms in reversible covalent DDNs

- *Work summary: period 1/11/2017 → 31/10/2018*

Started data: 1st September 2018. My work could be summarized as follows.

Study:

Initial approach to the basic fields of Rheology, Rheometry and Polymers.

The main reference books are:

Rheology Principles, Measurements And Applications (C. W. Macosko)

Polymer Physics (M. Rubinstein, R.H. Colby)

Various Articles

Training:

Learning how to use different rheometers and geometries according to the tests to perform and how to evaluate the fundamental parameters of the sample from the obtained data.

Understanding the preparation of different samples according to their characteristics properties.

Linear and Non Linear Measurements. These tests were performed using Polystyrene with different weight-average molar masses in order to compare the data obtained. Linear Tests were conducted using two different geometries, Plate-Plate and Cone-Partitioned Plate. The latter, which generates a constant deformation inside the sample, was also used for Non Linear measurements.

The Linear Tests were conducted in order to investigate the viscoelastic response of samples. In particular, was applied the principle of Time-Temperature-Superposition to extend the time or frequency regime. In fact, temperature variation moves the viscoelastic functions along the time without altering their shapes. Moreover, Van-Gurp-Palmen-plot was used to verify the Time-Temperature-Superposition principle.

Initial approach to the Non Linear measurements to understand the response of the viscosity and stress of the samples in transient conditions.

- *Deliverable and Milestones*

D3.8a Nonlinear shear behavior of new DDNs (FORTH)

D3.8b Fracture mechanisms and self-healing properties of new DDNs (FORTH)

D5.8b Relating fracture mechanisms and adhesive properties (ESPCI)

D5.8b Designing new reversible covalent DDNs for enhanced mechanical properties (Tesa)

- *Publications and conferences*

N/A

- *Courses followed*

Generalities on networks (Giuseppe Marrucci, UN)

Introduction to Polymer Synthesis (Renaud Nicolaÿ, ESPCI)

Introduction to supramolecular polymers (Charles-André Fustin, UCLouvain)

Basic Polymer Science (Daniel Read, ULeeds)

Curing chemistry of organic coating systems (Patrice Roose, Allnex)

Introduction to scattering theory (Daniel Read, ULeeds)

Introduction to Scattering Techniques (Benoit Loppinet, FORTH)

Basic molecular rheology (linear regime) (Dimitris Vlassopoulos FORTH)

High shear (Dimitris Vlassopoulos FORTH)

Introduction to extensional rheology (Qian Huang, DTU)

Double Dynamic Networks: a review (Evelyne van Ruymbeke, UCLouvain)

Basic principles of coarse-grained molecular simulations (Giovanni Ianniruberto, UN)

Microscopic dynamics and rheology of soft gels: computational approaches and connection to experiments (Emanuela Del Gado, Georgetown University)

- *Exchange visits*

N/A

9. ESR Annual Report – Year 1 : ESR 9 Simone Sbrescia

- *ESR*

Simone Sbrescia, ESR 9, Influence of Temperature and composition on mechanical properties of DD-thermoplastic elastomers

- *Work summary: period 1/11/2017 → 31/10/2018*

The project started in May with deep study of the state of the art on thermoplastic elastomers by means of their composition, structure and mechanical behavior. In parallel I was also looking at the different methods to run fracture tests on gel-like materials or rubber to find the best way to evaluate the fracture behavior of thermoplastic elastomers.

I learnt how to prepare the samples to test by using a hot press which allowed me to prepare thin films from pellets; tensile bars were then punched out from those films in order to be tested.

A training session for the use of tensile machines started and after that I run tensile tests on a model system based on six different samples with same chemistry but different ratio between soft block and hard blocks as well as a different thermal history (annealing). The test was done in order to assess the influence of composition on mechanical properties, in particular strain at break, first at room temperature and then at 5 different temperature (from 50 to 150 Celsius

degrees) since it has been seen for thermoplastic elastomers a dramatic drop of strain at break by increasing temperature.

Cyclic tests were also conducted on this system to get more clues about the structural transition that happen during stretching both at room and higher temperature by varying the composition of the materials.

The mechanical tests run at different temperature were coupled with thermal analysis by means of DSC (Differential Scanning Calorimetry) and DMA (Dynamic mechanical Analysis) in order to build up a better picture of the behavior of these material at different temperature when the composition and the thermal history changes. It was also interesting to see how the soft block/hard block ratio and annealing influence the melting point of the material and whether they make other thermal transitions appear.

Different tests with different sample's shapes and methods are running to assess the best protocol to run fracture tests on these materials.

Mechanical tests at different temperature were also conducted as above on a model system based on two different composition (same chemistry, different soft block/ hard block ratio), same soft block and hard block length, but with five different molecular weight to see whether the molecular weight influences the strain at break at higher temperature of these materials as well as the general shape of the stress-strain curve and the hardening in the high strain regime. As for the previous model system DSC and DMA are planned to be conducted on this system as well as cyclic tests to see whether the structural transition within the material appear and how with different molecular weight at temperature higher than room temperature.

▪ *Deliverable and Milestones*

D3.9 Mechanical properties of DD-TPEs 3 : (Ongoing) Tensile Test and Cyclic tests on two different model systems at different temperature coupled with thermal analysis (DSC and DMA).

D2.9 Influence of the DD-TPEs composition on the structure of crystallites

D4.9 Statistical composition of DD-TPEs and relation to rheology: Planned to be done in January

D5.9 Relating fracture process to mechanical properties of DDNs: (Ongoing) Finding a good way to test and characterize the fracture mechanics of thermoplastic elastomers.

- *Publications and conferences*

NA

- *Courses followed*

Introduction to polymer synthesis

Introduction to supramolecular polymers

Curing chemistry of organic coating systems

Introduction to scattering theory

Introduction to scattering techniques

Basic molecular rheology (linear regime and high shear)

Introduction to extensional rheology

Basic principles of coarse-grained molecular simulations

Microscopic dynamics and rheology of soft gels: computational approaches and connection to experiments

RPK-B Polymer Dynamics

- *Exchange visits*

Laboratories visit in FORTH during the meeting

Laboratories visit in UCLouvain several times

10. ESR Annual Report – Year 1: ESR 10 Paola Nicolella

- *ESR*

Paola Nicolella ESR (10) - Structure and diffusion in DDN at the nano- to micro- scale

- *Work summary : period 1/11/2017 → 31/10/2018*

The following work summary refers to the period of September and October 2018. Introduction to the safety procedures of the laboratories and a safety instruction lesson about lasers have been given, as requested from the hosting University. Literature about polymer networks, defects, heterogeneities and how to characterize them

have been read. Particular attention has been given to Dynamic and Static Light Scattering, Fluorescence Recovery after Photobleaching, Rheology.

Presentation for the Project Meeting in Crete has been prepared and discussed. Participation in the Project Meeting and in the Elementary Modules I in Crete. First experiments with light scattering: how to prepare the probe, how to clean the cuvettes, use of the machine. Particular attention is given to the theory of scattering.

▪ *Deliverable and Milestones*

Deliverable Number	Deliverable Title	WP	Lead Beneficiary	Type	Dissemination Level **	Due Date*
D2.10a	Mesh size, phase-separated domains and homogeneity of model DDN	2	UM (ESR 10)	Report	Public	M24
D2.10b	Time evolution and equilibrium state of phase-separated domains and their influence on the diffusion coefficient	2	UM, FORTH (ESR 10)	Report	Public	M32
D1.10	Study the influence of synthesis protocol on the structure of DDNs	1	UCL (ESR 10)	Report	Public	M34
D5.10a	Role of heterogeneities on application properties of the DDNs	5	UM, ESPCI (ESR 10)	Report	Public	M40
D5.10b	Importance of structure and diffusion in coating applications	5	Allnex (ESR 10)	Report	Public	M42

D2.10a Mesh size, phase-separated domains and homogeneity of model DD

Study of the methods by which the mesh size can be determined. How it can be experimentally extracted. Which is the physical meaning and the difference with the one calculated theoretically with the Einstein equation. Influence of the form factor on the mesh size.

- *Publications and conferences*

No publications have been written and no conferences have been attended in the period September-October 2018.

- *Courses followed*

- Elementary Modules I (FORTH) September 2018
- Physical Chemistry of Polymers (University of Mainz) October 2018

- *Exchange visits*

The laboratories of FORTH have been visited in September within the Elementary Modules I.

11. ESR Annual Report – Year 1: ESR 11 Hongwei Liu

- *ESR*

Hongwei Liu, ESR#11, Topic: Modeling the Nonlinear Rheology of Reversible Double Dynamics Networks.

- *Work summary : period 1/11/2017 → 31/10/2018*

I started this program on 3rd, September 2018. Besides, it's my first time living in overseas. Getting used to the local life costs me a few days. Therefore, up to now, I haven't conducted too much relevant research works. Here I primarily record some gains in science.

Shortly after arriving Naples, I flew to Crete to attend our first meeting. In this meeting, professor Giovanni Ianniruberto's lecture impressed me most. His topic is *Basic Principles of Coarse-Grained Molecular Simulations*. First, he introduced two main simulation approaches to us-- Molecular dynamics (MD) and Monte Carlo (MC). While MC methods is only useful for equilibrium dynamics, i.e., for linear rheology, MD methods also have some disadvantages. For

example, the time steps typically used in MD methods are usually not compatible with polymer relaxation times. That is why we should study the rheological behaviors of polymers using coarse-grained molecular simulation methods. Starting from the simplest dynamics: Brownian particles with 1 degree of freedom, professor Giovanni showed us the derivation process of mass balance equation. Then he put an emphasis on the Langevin equation, which actually is a force balance equation. Recently, I programed Fortran language to solve these two equations separately and compared the results. It turned out that the final results are equal with each other in fact. Except the Langevin methods, the Smoluchowski approach was also discussed. It mainly has these three features: 1) Solution of the Smoluchowski equation is seldom analytic, though an analytic solution may become possible after some approximation is introduced. Numerical solution is the alternative. 2) Once End-to-end vector distribution function) is obtained, all averages can be calculated, among them the average that corresponds to the stress tensor. 3) Sometimes, the partial differential equation for Ψ is transformed (by a suitable integration over the whole space of the coordinates) into a much simpler ordinary time-differential equation for the stress tensor, usually through simplifications called “closure approximations”. These two methods both have advantage and disadvantage: 1) For the dumbbell case, the Smoluchowski approach is preferred since we can analytically determine rheologically- relevant observable in view of the equation linearity. 2) If, for instance, we want to account for finite extensibility effects of the polymer chain, the force becomes nonlinear and the Langevin approach is preferred. Next, he further explained these two methods by applying them to the Dumbbell model. Finally, professor displayed some research results. Professor Giovanni’s straightforward lecture help me enter the world of simulation quickly.

▪ *Deliverable and Milestones*

Not yet.

Deliverable Number	Deliverable Title	WP	Lead Beneficiary	Type	Dissemination Level **	Due Date*
D4.11a	Multiple dynamics in reversible DDNs	4	UN (ESR 11)	Report	Public	M24
D4.11b	Modelling the nonlinear viscoelastic properties of sticky DDNs	4	UN (ESR 11)	Report	Public	M38
D4.11c	Influence of chain	4	DTU (ESR 11)	Report	Public	M40

	stretching on the lifetime of reversible properties					
D5.11	Relating chain stretching and strain hardening to adhesive properties	5	tesa (ESR 11)	Report	Public	M45

▪ *Publications and conferences*

Not yet.

▪ *Courses followed*

Introduction to Polymer Synthesis	Renaud Nicolaÿ, ESPCI	2h
Introduction to supramolecular polymers	Charles-André Fustin, UCLouvain	1h30
Basic in polymer physics	Daniel Reed, ULeeds	0h45
Curing chemistry of organic coating systems	Patrice Roose, Allnex	1h50
Introduction to Scattering Theory	Daniel Reed, ULeeds	1h30
Introduction to Scattering Techniques	Benoit Loppinet, FORTH	1h30
Basic molecular rheology	Dimitris Vlassopoulos, FORTH	1h30
High shear	Dimitris Vlassopoulos, FORTH	1h
Introduction to extensional rheology	Qian Huang, DTU	1h30
Double Dynamic Networks: a review	Evelyn van Ruymbeke, UCLouvain	1h
Basic principles of coarse-grained molecular	Giovanni Ianniruberto, UN	1h30
Microscopic dynamic and rheology of soft gels: computational approaches and connection to experiments	Emanuela Del Gado, Georgetown University	2h

- *Exchange visits*

19/Sep-26/Sep/2018 Visiting the Foundation for Research and Technology - Hellas (FORTH), Heraklion, Greece.

12. ESR Annual Report – Year 1: ESR 12 Yanzhao Li

- *ESR*

Name: Yanzhao Li

Number and title of research: ESR12, modelling the linear dynamics of Double Dynamics Polymer Networks

- *Work summary : period 1/11/2017 → 31/10/2018*

I started the project from September 11th, 2018 and do not have any practical results for the moment. I attended the first meeting, elementary modules on double dynamic networks, in Crete, Greece from 21st to 26th, September and made a presentation introducing my coming work, as well as had some courses.

Cooperating with other ESR partners, my objective of the project is to investigate and model 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. My beginning work plan is shown as below:

① ***Bibliographic research and elaboration of a tube model*** for describing the rheology of entangled polymers: A comprehensive literature review is required about the dynamics of entangled supramolecular polymers and about the properties of DDNs. Meanwhile, I will receive a training on tube models and will prepare my own code based on the expertise of our group.

② ***Rheometry: Determining the statistical composition of the sticky chains***, I will measure specific sets of samples, which will help understanding the influence of their composition parameters.

③ **Modelling:** *Determining a strategy to describe my experimental data*, I will work on developing a model to determine the rheology of entangled sticky chains, and including the sticker dynamics in my tube model. If necessary, new samples will be designed in order to answer specific questions that need to be addressed for the modeling part.

In order to model their viscoelastic behavior, before the work of DDNs, I will start from the tube model developed at our group to predict the properties of supramolecular entangled polymers. I am now reading literatures about tube model and double networks, and start to work based on the research work of a lab colleague, who has done a lot on metallo-supramolecular polymer. Two different metal ions(selected from Zi^{2+} , Co^{2+} , Cu^{2+} and Ni^{2+}) will be blended in the same sample, for example, Zi^{2+} and Co^{2+} are selected as metal ions to associated with ligand of four-arm telechelic star PnBA-tpy₄, to investigate the influence of various ratios on the rheological behavior, and determine their specific contribution to the viscoelastic properties. The effect of external stimuli such as elongation, shear and temperature on the dynamic responses of the blends will also be studied.

▪ *Deliverable and Milestones*

Deliverable Number	Deliverable Title	WP	Lead Beneficiary	Type ***	Dissemination Level **	Due Date*
D4.12a	Statistical tools to determine the composition of DDNs	4	UCL (ESR 12)	SW	Public	M20
D4.12b	Modelling the linear rheological properties of DDNs	4	UCL (ESR 12)	Report	Public	M32
D2.12	Modelling the diffusion processes in DDNs	2	UM (ESR 12)	Report	Public	M34
D5.12	Statistical tools for the design of DDNs for coating applications	5	Allnex (ESR 12)	Report	CO	M39

D4.12c	Software available for predicting the LVE of DDNs	4	UCL (ESR 12)	SW	CO	M44
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* Taking into account that the starting month is November 2017

**CO= public only after the agreement of the industrial Partner

*** SW = Software

▪ *Publications and conferences*

The conferences in Crete, Greece on 21st to 26th, September, 2018

I attended the first conferences of the Dodynet project: elementary modules on double dynamic networks, and made a presentation introducing my coming work, as well as had some courses.

▪ *Courses followed*

Introduction to Polymer Synthesis, **Renaud Nicolaÿ**, ESPCI

Introduction to supramolecular polymers, **Charles-André Fustin**, UCLouvain

Curing chemistry of organic coating systems, **Patrice Roose**, Allnex

Introduction to scattering theory, **Daniel Read**, ULeeds

Introduction to Scattering Techniques, **Benoit Loppinet**, FORTH

Basic molecular rheology (linear regime), **Dimitris Vlassopoulos**, FORTH

High shear, **Dimitris Vlassopoulos**, FORTH

Introduction to extensional rheology, **Qian Huang**, DTU

Double Dynamic Networks: a review, **Evelyne Van Ruymbeke**, UCL

Basic principles of coarse-grained molecular simulations, **Giovanni Ianniruberto**, UN

Microscopic dynamics and rheology of soft gels: computational approaches and connection to experiments, **Emanuela Del Gado**, Georgetown University

- *Exchange visits*

During the first conference of DoDyNet project, on 25th September, 2018, we visited the Lab of Forth, University of Crete, Greece.

13. ESR Annual Report – Year 1: ESR 13 Jianzhu Ju

- *ESR*

Jianzhu Ju, ESR 13

Application property of double dynamic polymer networks

- *Work summary : period 1/11/2017 → 31/10/2018*

In the first two months of my project, the objectives are learning about diffusing wave spectroscopy (DWS) technology and prepare for the experimental material/set-up. Also, fracture property of TPEs material (block copolymer of poly (butylene terephthalate) and polytetrahydrofuran (PBT/PTHF)) from DSM will be investigated taking the advantage of DoDyNet collaboration (WP7). I have attended the intermediate meeting in Crete, Greece and elementary module.

1. DWS testing on fracture property

For starting, we are planning to applied DWS to PDMS (Polydimethylsiloxane) as a model material. PDMS sample is prepared from Sylgard 184 Silicone Elastomer Kit. The sample dimension is 20 mm*50 mm with thickness controlled by different amounts of elastomer and curing agent (10:1). To achieve that, an aluminum mold is designed and fabricated, as seen in Fig. 1. The maximal thickness in the mold is 10 mm. After the right size of PDMS and successful addition of nanoparticles, other double dynamic network will be further studied. The selection of the nanoparticles and preparation process also need to be further discussed. For DWS technology training, water with the addition of nanoparticles with the diameter of 500 nm was studied with DWS.

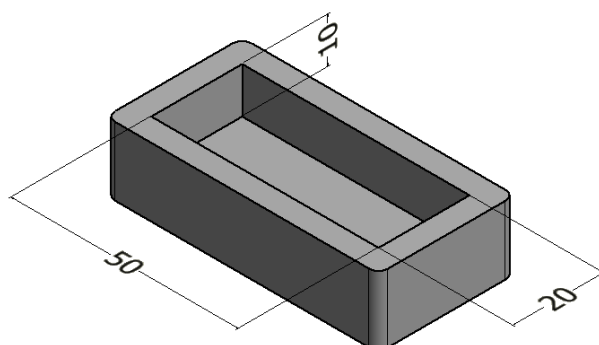


Fig. 1 The design of aluminum mold.

2. Fracture property of TPEs material

TPEs materials have been ordered from DSM company. Samples with different concentrations of PBT will be applied to study the contribution of different components. Various preparation methods (Solvent casting and hot pressing) from commercial TPEs will be applied to find out the proper approach to fracture investigation.¹ After the preparation of TPEs sample, fatigue testing and regular fracture testing will be performed first to study the fracture property of the material. Fatigue set-up experiments on model material has been performed for set-up training.

1. Nébouy, M.; de Almeida, A.; Brottet, S.; Baeza, G. P., Process-Oriented Structure Tuning of PBT/PTHF Thermoplastic Elastomers. *Macromolecules* **2018**, 51 (16), 6291-6302.

■ Deliverable and Milestones

Deliverable Number	Deliverable Title	WP	Lead Beneficiary	Type	Dissemination Level **	Due Date*
D5.13a	Fracture mechanisms in DD-TPEs	5	DSM (ESR 13)	Report	CO	M24
D5.13b	Fracture mechanisms in model DDNs	5	ESPCI (ESR 13)	Report	Public	M32
D5.13c	Adhesive and self-adhesive properties of reversible covalent DDNs	5	ESPCI (ESR 13)	Report	Public	M36

D4.13	Relating fracture properties to elasto-capillarity	3	CNRS (ESR 13)	Report	Public	M36
D5.13d	Mechanical and adhesive properties of slide-ring DDNs	5	ESPCI (ESR 13)	Report	Public	M44

- *Publications and conferences*

NA.

- *Courses followed*

Elementary module in Dodynet.

- *Exchange visits*

We welcomed Prof. Luca Cipelletti from Laboratoire Charles Coulomb, Université Montpellier. We discussed about DWS technology and Dodynet experiments.