

# KINETICS OF GELATION IN pH/TEMPERATURE-SENSITIVE HYDROGELS SYNTHESIS

Virginia Pinto<sup>1</sup>, Miguel Gonçalves<sup>1</sup>, Rolando Dias<sup>1</sup> and Mário Rui Costa<sup>2</sup>

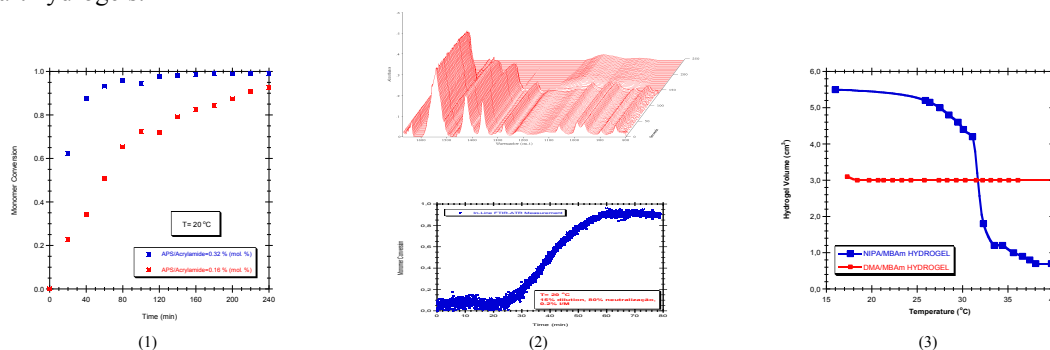
<sup>1</sup>LSRE - Polytechnic Institute of Bragança, Campus de Santa Apolónia  
Apartado 1134, 5301-857 Bragança, Portugal

<sup>2</sup>LSRE – Fac. Eng. University of Porto, Dep. Eng. Química, R. Roberto Frias  
4200-465 Porto, Portugal

## Abstract

Kinetics of gelation was experimentally and theoretically studied for different polymerization systems leading to the formation of pH/temperature-sensitive hydrogels. Acrylamide (AAm), N-isopropylacrylamide (NIPA), N,N-dimethylacrylamide (DMA), acrylic acid (AA), methacrylic acid (MAA) were used as main monomers, and N,N'-methylenebisacrylamide (MBAm) as crosslinker. Stirred batch reactor polymerizations were performed in aqueous media using mostly inverse-suspension operation at 200 mL total reaction volume. Sampling was performed along the reaction time allowing the study of the dynamics of gel formation. Classical free radical polymerization (FRP), with initiation by ammonium persulfate (APS), and RAFT polymerization with 2-dodecylthiocarbonothioylthio-2-methylpropionic acid (DDMAT) were considered. Different parameters were changed along the experimental program, namely the kind and initial concentrations of the different monomers involved (crosslinking copolymerizations and terpolymerizations were considered) and the initial molar ratio initiator/DDMAT/monomer. Intermediate and final products were characterized by size exclusion chromatography, running directly with aqueous eluent, with simultaneous detection of refractive index and multi-angle laser light scattering (SEC/RI/MALLS). Kinetics of monomer consumption and molecular architecture of the soluble phase were thus measured. Kinetics of polymerization was also investigated through *in-line* FTIR-ATR. Sensitivity of the hydrogels synthesized to pH, temperature and pH/temperature changes was also experimentally assessed.

Kinetic modeling studies on network formation in these different chemical systems were performed in the framework of a general kinetic theory for non-linear polymerization.<sup>(1)-(4)</sup> A polymer reaction engineering approach is thus considered in order to develop computational tools linking the synthesis conditions with end-use properties of smart hydrogels.



(1): SEC measured time-evolution of monomer conversion during the inverse-suspension copolymerization of AAm/MBAm at 20 °C with 5% monomer dilution in water. Results for two different initial mole ratios APS/AAm are shown. (2): Typical *in-line* FTIR-ATR spectrum observed during the aqueous polymerization of acrylic acid. The bottom figure shows the *in-line* measured monomer conversion of AA at 20 °C, 15% dilution, 80% neutralization and 0.2% APS/AA. (3): Measured temperature-sensitivity of inverse-suspension synthesized NIPA/MBAm and DMA/MBAm hydrogels. Both hydrogels were obtained by crosslinking polymerization at 20 °C with 10% monomer dilution in water.

## Acknowledgements

Financial support by Fundação para a Ciência e a Tecnologia (FCT), Ministry of Science and Technology of Portugal (Program COMPETE - QCA III) and European Community through FEDER is gratefully acknowledged (project PTDC/EQU-EQU/098150/2008).

## References

- (1) Costa, M.R.P.F.N.; Dias, R.C.S. *Chem. Eng. Sci.* **2005**, *60*, 423.
- (2) Dias, R.C.S.; Costa, M.R.P.F.N. *Polymer* **2006**, *47*, 6895.
- (3) Costa, M.R.P.F.N.; Dias, R.C.S. *Polymer* **2007**, *48*, 1785.
- (4) Gonçalves, M.A.D.; Pinto, V.D.; Dias, R.C.S.; Costa, M.R.P.F.N. *Macromol. Symp.* 2011, 306-307, 107.]

# Polymer Networks 2012

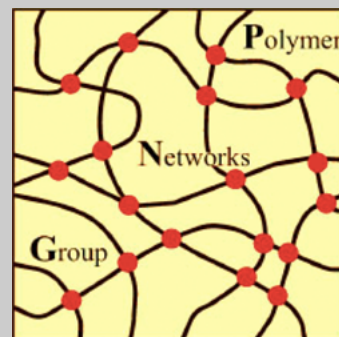
August 12-16  
Jackson Hole, WY, USA

Welcome

## Menu

- Welcome
- Plenary Lectures
- Keynote Lectures
- Technical Program
- Short Course
- Registration
- Paper Submission
- Accommodations
- Activities
- Contact
- About PNG

The Polymer Networks Group would like to welcome you to participate in the Polymer Networks 2012 Conference. This meeting will encompass a wide range of topics, including but not limited to Biomaterials, Reversible Networks, Fundamental Formation-Structure-Property Relationships, Composite Networks, Smart and Responsive Networks, and Novel Network Formation Strategies and Reactions.



The 2012 Conference will be held in scenic [Jackson Hole](#), Wyoming, USA at the [Snow King Resort](#). This is just a 15 minute shuttle ride from the [Airport](#), which has a range of non-stop flights from most major U.S. airports. Jackson Hole is just south of the [Teton](#) and [Yellowstone](#) National Parks and near a myriad of shopping, site seeing, and outdoor activities.

The conference will feature short courses, plenary talks, parallel sessions, posters, and extensive activities.



Tuesday, August 14

---

Poster Session I

4:00 – 5:30

- 1 Ricardo Acosta Ortiz  
*Development of Thiol-Ene/Epoxy-Amine Photocurable Systems*
- 2 Alan Aguirre Soto  
*Hydrogen Bonded Pseudo Cross-linked Networks from Acrylic-based Monomers: Kinetic Effect*
- 3 Abeer Alzahrani  
*Photo-mediated CuAAC reaction: Capabilities and Applications*
- 4 Kentaro Taki  
*Kinetic Analysis of Photopolymerization of Mono- and Di- functional Methacrylate Group Monomer Mixtures using Real Time FT-IR*
- 5 JianCheng Liu  
*Photo-Reactive Nanogel for Tuning Properties during Polymer Network Formation*
- 6 Detlef Reichert  
*Synthesis and Characterization of Well Defined PEG networks by “Click” chemistry*
- 7 Shunsuke Chatani  
*Vinyl Sulfone as a Component of Two-Stage Curing Polymer Systems*
- 8 Megan Cole  
*Synthesis and Characterization of Thiol-Ene Functionalized Siloxanes and Evaluation of their Crosslinked Network Properties*
- 9 Rolando Dias  
*Kinetics of Gelation in pH/Temperature-Sensitive Hydrogels Synthesis*
- 10 Rolando Dias  
*Reversible Addition-Fragmentation Chain Transfer Copolymerization of Styrene/Divinylbenzene in Aqueous Suspension*
- 11 Christopher Fenoli  
*Advances in RAFT Monomer Development*
- 12 Tao Gong  
*Bulk Photopolymerization Using Photo Induced Copper (I)-Catalyzed Alkyne-Azide Cycloaddition (CuAAC)*
- 13 Weixian Xi  
*Nitrogen-centered Nucleophile Catalyzed Thiol Vinylsulfone Addition, another Thiol-ene “Click” Reaction*
- 14 Pelin Yazgan Birgi  
*Modification of Polystyrene as a Coating Material via Sunflower Fatty Acid*
- 15 Sophie Bistac  
*Emulsion Stabilization by Polymeric Surfactants: Influence of Nanogels Formation on Colloidal and Interfacial Rheological Behaviours*
- 16 Maurice Brogly  
*Nanoscale Adhesion Release Properties of PDMS Networks Investigated by Atomic Force Microscopy*
- 17 Matthew Barros  
*Chain length, Branching, and (Meth)Acrylate Functionality in Polymerization Induced Phase Separation*
- 18 James Goetz  
*Network Behavior Investigation of Tunable, Highly Permeable, UV-Cured, Perfluorinated Acrylate Modified Thiol-ene Networks*
- 19 Rouven Henkel  
*The Influence of RAFT on the Elastic Properties of UV-initiated Statistical Poly-butyl-acrylate Networks*
- 20 Jongshin Park  
*Preparation of Thermoplastic Polyurethanes using Partially Acetylated Lignin*
- 21 Yoshimi Seida  
*QCM Observation of Viscoelastic Behavior of Collapsed Poly(NIPAm) Gel in Response to Protein Adsorption*

- 22           Yongsok Seo  
*Foaming of Recycled Crosslinked Polyethylenes via Supercritical Decrosslinking Reaction*
- 23           Caroline Szczepanski  
*Design of Low Shrinkage, Heterogeneous Networks via Polymerization-Induced Phase Separation*
- 24           James Wydra  
*Property Development in Photopolymerizations*
- 25           Bernd Lauke  
*Structure Evolution of Carbon Black Networks in Elastomers Under Deformation*
- 26           Ryan Guterman  
*Ultra-High Loading of Phosphonium Cations in UV-Cured Films: Accessing the Surfaces Charges for Layer-By-Layer Assembly Applications*
- 27           Delia Lopez Velazquez  
*Networks of Poly(bis-allylcarbonate of Dihydroxybenzaldehyde*
- 28           Sara Aßhoff  
*Stabilizing Photochromic Liquid Crystals with Polymer Networks*
- 29           Cigdem Tasdelen Yucedag  
*Modification of Polystyrene with Polycaprolactone via Click Chemistry*
- 30           Soon Man Hong  
*Recycling of Cross-linked Low Density Polyethylene (LDPE) Using Extrusion Process*
- 31           Sini NK  
*Effect of Blending on Thermal Behavior of Cardanol Based bisbenzoxazine Monomers and Bisimides*

Wednesday, August 15

---

Poster Session II

4:00 – 5:30

- 1 Ming Gao  
*High Resolution Monitoring of Hydrogel Swelling: Enhancing Swelling Kinetics of DNA-polymer Hybrid Hydrogel Employing Polyethyleneglycol as a Porogen*
- 2 Ethan Gillett  
*Allyl Sulfide Containing Covalent Adaptable Networks (CANs) Properties and Applications*
- 3 Takehiko Gotoh  
*Repeated Adsorption of Metal Ions onto Thermosensitive Ionic Hydrogel by Temperature Swing*
- 4 Devatha Nair  
*Two-Stage Reactive Polymer Materials Platform*
- 5 Jing Zhou  
*Acoustic Activation of Shape-Memory Materials*
- 6 Gayla Berg  
*2D and 3D Photolithography Using Diels-Alder and Thiol-Ene Click Reactions*
- 7 Jessalyn Cortese  
*Organization in Supramolecular Polymers*
- 8 Mathieu Capelot  
*Vitrimers: Silica-Like Malleable and Weldable Thermosets*
- 9 Clémence Wable  
*Mechanical and Thermodynamic Characterization of Hybrid PDMA Hydrogels*
- 10 Jennifer Macron  
*Reversible Adhesion of Hydrogels in Aqueous Media*
- 11 Kenneth Koehler  
*Diels-Alder Mediated Controlled Release from a PEG Based Hydrogel*
- 12 Junkal Gutierrez  
*Simple-Route to Fabricate Smart Nanopapers Based on Bacterial Cellulose and Different Inorganic Nanoparticles*
- 13 Jennifer Leight  
*Characterizing MMP Expression using Modular Fluorescent Peptide Biosensors*
- 14 Katherine Lewis  
*Formation of Model Alveoli In A Tunable Synthetic Scaffold*
- 15 Vijay Mannari  
*UV-curable Polyurethane Dispersions based on Acrylated Soy-polyols: Fine Tuning Network Structure, Bio-renewable Content and Performance Properties of Coatings*
- 16 Emily Matherly  
*Thiol-ene Hydrogels Can Maintain Stem Cell Pluripotency in a Precisely Controlled Niche*
- 17 Dagmara Smith Motriuk  
*Araneus Gemmoides Dragline Silk*
- 18 Helina Pohjanlehto  
*Lignin Based Polymer Network Systems: Preparation and Characterization*
- 19 Kelly Pollock  
*Manipulating the Microenvironment to Control Valvular Interstitial Cell Phenotype*
- 20 Raveesh Shenoy  
*3-D Conformal Coatings by Interfacial Radical Polymerization Initiated by a Glucose Oxidase-Mediated Redox System*
- 21 Jędrzej Skrobot  
*In Vitro Degradation of Photo-Cross-Linked Elastomeric Networks for Soft Tissue Regeneration*
- 22 Jędrzej Skrobot  
*Gamma Radiation Induced Grafting of 1-Vinyl-2-Pyrrolidone (NVP) on Multiblock Polyesters*
- 23 Bradley Sparks  
*Structure-Property Relationships of Dopamine Acrylamide Modified Thiol-Ene Networks*

- 24** Felicia Svedlund  
*A Synthetic Polymer-based, Micropatterned Surface for the Culture of Embryonic Stem Cells*
- 25** Emi Tokuda  
*Understanding the Role of the Microenvironment in Melanoma Responses to MEK Inhibition*
- 26** Kelly Trowbridge  
*Acrylate and Thiol-Ene PEG Hydrogels for Islet Encapsulation*
- 27** Redouan Mahou  
*Encapsulation of Cells Within Hybrid Microspheres*
- 28** Eric Dailing  
*Network Modification through Water-Dispersable Nanogels*
- 29** Steven Lewis  
*Synthesis and Polymer Network Development of Water-compatible Nanogels using Conventional Hydrophobic and Hydrophilic Monomer Combinations*
- 30** Hernane Barud  
*Bacterial Cellulose/Silk Fibroin Sponge Scaffold*
- 31** Stevin Gehrke  
*Structure-Function Properties of Beetle Elytral Cuticle, a Multicomponent Biomaterial*