# REVERSIBLE ADDITION-FRAGMENTATION CHAIN TRANSFER COPOLYMERIZATION OF STYRENE/DIVINYLBENZENE IN AQUEOUS SUSPENSION

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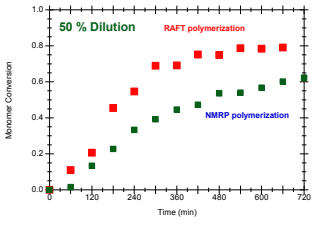
**Abstract**

The Reversible Addition-Fragmentation Chain Transfer (RAFT) copolymerization of styrene (S) and divinylbenzene (DVB) was performed at temperature range 110 to 150 °C in aqueous suspension, using AIBN as thermal initiator and 2-dodecylthiocarbonothioylthio-2-methylpropionic acid (DDMAT) as RAFT agent. A pressurized stirred reaction vessel with 1 L capacity was used. Sampling was performed at different reaction times, thus allowing the measurement of the dynamics of monomer conversion and gel formation. The soluble fraction of these samples was analyzed by size exclusion chromatography with simultaneous detection of refractive index and multi-angle laser light scattering (SEC/RI/MALLS). Reaction-time evolution of molecular weights and *z*-average radius of gyration was thence measured before and after gelation. The concentration of pendant double bonds (PDB) present in the network structure was also measured trough iodine chloride titration. Operation parameters such as the reaction temperature, initial mole ratio DDMAT/AIBN, amount of DVB in monomer mixture and dilution of the monomers in the organic phase were changed along the experimental program. In order to analyze the impact of the polymerization technique used on the structure of the networks, similar free radical (FRP) and nitroxide mediated radical polymerization (NMRP) runs were also performed.

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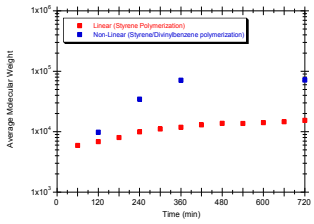


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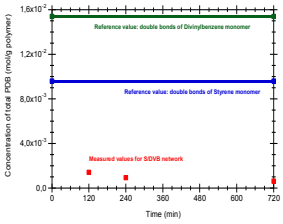


(3)

(1): Time evolution of monomer conversion during the aqueous suspension RAFT polymerization of S/DVB at 130 °C (DDMAT/AIBN=2). Results for a similar NMRP run are also shown. (2): Measured molecular weight dynamics during the aqueous suspension RAFT polymerization of S and S/DVB. Both runs at 130 °C with DDMAT/AIBN=2. (3): Measured dynamics of PDB concentration (mol PDB/g polymer) during the RAFT S/DVB copolymerization with 5% DVB in the monomer mixture.

This experimental program is accompanied by kinetic modeling studies aiming at the prediction of key features of S/DVB network formation. A general kinetic approach[(1)-(4)] allowing the calculation of molecular weight, *z*-average radius of gyration and sequence lengths is considered. Prediction capabilities of the kinetic models are assessed trough the comparison with experiments. Mechanistic dissimilitude between RAFT, NMRP and FRP and also the impact of the synthesis technique considered on the molecular architecture of the networks is thus studied. Non-ideal crosslinking (e.g. intramolecular cyclization) is investigated and a few engineering rules are established to design polymer networks with enhanced structural homogeneity.

**Acknowledgements**

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**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.; Dias, R.C.S.; Costa, M.R.P.F.N. *Chem. Eng. Technol.* **2010**, *33*, 1797.


# Welcome

Menu

Welcome
Plenary Lectures
Keynote Lectures
Technical Program
Short Course
Registration
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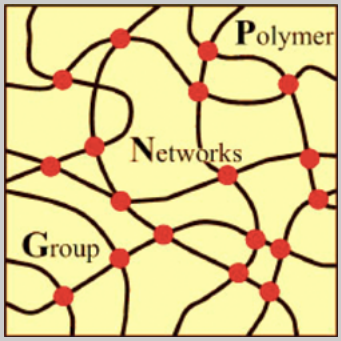
About PNG

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
*Modıfıcatıon of Polystyrene as a Coating Material vıa 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 Viscoeleastic Behavior of Collasped 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** Jedrzej Skrobot
*In Vitro Degradation of Photo-Cross-Linked Elastomeric Networks for Soft Tissue Regeneration*

**22** Jedrzej 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 Modificaiton 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*