KINETICS OF GELATION IN pH/TEMPERATURE-SENSITIVE HYDROGELS SYNTHESIS

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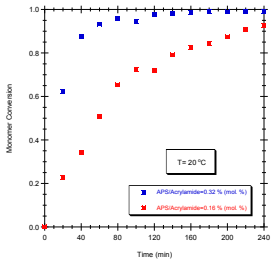
Abstract

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.(1)-(4) 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.



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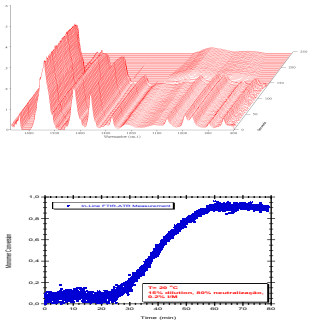

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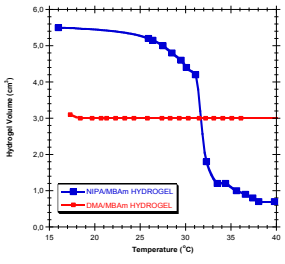

(3)

(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 showed. (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

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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.; Pinto, V.D.; Dias, R.C.S.; Costa, M.R.P.F.N. Macromol. Symp. 2011, 306-307, 107.]

Welcome

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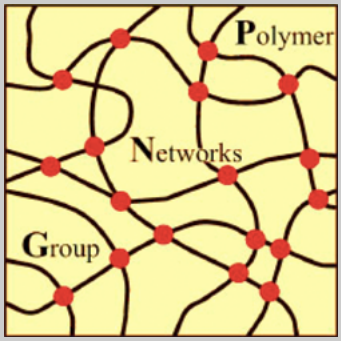
About PNG

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