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Fundamentals of Gels and Self-Assembled Polymer Systems

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Fundamentals of Gels and Self-Assembled Polymer Systems

PREFACE

This volume contains the Proceedings of Symposium E, "Fundamentals of Gels and Self-Assembly Systems", from the 2013 MRS Fall Meeting held December 1-6, 2013 in Boston, Massachusetts.

The symposium focused on the most recent advances of the following topical categories: network formation and characterization, structure-property relationships in synthetic and biopolymer gels, self-assembly of biopolymers, responsive gels, nanostructures and composite materials. The symposium covered novel experimental tools and theoretical models to describe the behavior of various self-assembled systems. New insights were reported on the structure and dynamics of synthetic and biopolymer gels. This knowledge is essential for developing novel materials, improving and controlling material properties and performance. Several presentations were dedicated to the interface of polymer materials science with other fields, such as biomaterials and nanoscience. A number of papers dealt with the biomedical applications of gels (e.g., controlled release of antibiotics, tissue engineering). These applications require the creation of a well-defined microenvironment around the biologically active components to achieve the desired results. The papers in this volume illustrate the trends and recent progress in the field of supramolecular self-assembly and the important role of self-assembled structures in biomaterials science.

We would like to thank the staff at the Materials Research Society for their excellent work. We would also like to thank to all the contributors of this volume, authors and reviewers. We hope the volume will inspire for further developments in the field of polymer materials science.

Ferenc Horkay
Noshir Langrana
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May 2014

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CONTENTS

Preface ix

Materials Research Society Symposium Proceedings xi

* **Hierarchical Self-assembly of Microgel-modified Biomaterials Surfaces** 1
Yong Wu, Jing Liang, Qichen Wang, and Matthew Libera

* **Correlation between Mechanical Properties and Structure in Polymer Gels with Controlled Network Structure** 7
Takamasa Sakai, Yuki Akagi, and Ung-il Chung

Fabrication of Piezoelectric-rubber of Large Piezoelectric Property 17
Shogo Mamada, Naoyuki Yaguchi, Masanori Hansaka, Masafumi Yamato, and Hirohisa Yoshida

Effect of Methanol/Water Mixtures on the Lower Critical Solution Temperature of Poly(N-isopropylacrylamide) 25
Sanket A. Deshmukh, Ganesh Kamath, Derrick C. Mancini, and Subramanian K.R.S. Sankaranarayanan

Mechanical Properties of Polymer Gels with Bimodal Distribution in Strand Length 31
Shinji Kondo, Ung-il Chung, and Takamasa Sakai

Hydrogel Formation from the Concentrated Aqueous Solution of Polyvinyl Alcohol 37
Tomoyo Sakaguchi, Suong-Hyu Hyon, and Kazuaki Matsumura

* **Assessment of Functional Properties of Cartilage Using Double Quantum Filtered MRI** 41
Dan Benjamini, Uzi Eliav, Uri Nevo, Peter J. Basser, and Ferenc Horkay

*Invited Paper

Strong Tough Gels for 3D Tissue Constructs 49
Paul Calvert, Marc in het Panhuis, Geoffrey Spinks, Robert Gorkin, Leo Stevens, Shannon E. Bakarich, Paul Balding, and Damian M. Kirchmajer

Programmable Anisotropic Microparticles for Self-assembly Applications 55
Jonathan Liu, C. Wyatt Shields, Oluwatosin Omofoye, and Gabriel P. Lopez

Cartilage: Biomimetic Study of the Extracellular Matrix 61
Chinedu I. Anyaeji, Peter J. Basser, and Ferenc Horkay

* **Self-assembling Gels of a Hydrophobically Modified Biopolymer** 69
Pradeep Venkataraman, Joy St. Dennis, Rubo Zheng, Jaspreet Arora, Olasehinde Owoseni, Vijay T. John, and Srinivasa Raghavan

* **Tuning Mechanical Properties of Chondroitin Sulfate-based Hydrogels Using the Double-network Strategy** 79
Tiffany C. Suekama, Anahita Khanlari, and Stevin H. Gehrke

Supramolecular Self-assembly Inside Living Mammalian Cells 85
Yuan Gao, Ryan Nieuwendaal, Boualem Hammouda, Cristina Berciu, Daniela Nicastro, Jack Douglas, Bing Xu, and Ferenc Horkay

* **Quantitative Model for Clusters of String-like Cooperative Motion in a Coarse-grained Glass-forming Polymer Melt** 95
Beatriz A. Pazmiño Betancourt, Jack F. Douglas, and Francis W. Starr

* **Field-assembled Polymer Composites** 113
James E. Martin

Freezing Assisted Protein Delivery by Using Polymeric Cryoprotectant 123
Sana Ahmed and Kazuaki Matsumura

*Invited Paper

Phase Separation of Carboxylated Poly-L-lysine 129
Esha Das and Kazuaki Matsumura

* **Nanoprobe Diffusion in Poly(Vinyl-alcohol) Gels and Solutions: Effects of pH and Dehydration.** 135
Hacène Boukari, Candida Silva, Ralph Nossal, and Ferenc Horkay

Effects of Salt Concentrations on the Structural Transitions of Peptide-amphiphile Solution. 147
Takahiro Otsuka and Atsushi Hotta

Time Interval and Continuous Testing of Stimuli Responsive Hydrogels 153
Jeffrey S. Bates and Jules J. Magda

Rheological Characterization of Starch Gelatinization: Effects of Plasticizer/starch Ratio and Clay Content in Corn-starch/glycerol Thermoplastic Starch (TPS) 161
Sandra Lara and Felipe Salcedo

Investigation of Migration Behavior of Rod-like dsDNA in Gel with Precisely Controlled Network Structure. 169
Xiang Li, Kateryna Khairulina, Ung-il Chung, and Takamasa Sakai

Shear-thinning and Rapid-recovery Peptide Hydrogel for Biomedical Applications 175
Hongzhou John Huang and Xiuzhi Susan Sun

Mimicking the Extracellular Matrix: Tuning the Mechanical Properties of Chondroitin Sulfate Hydrogels by Copolymerization with Oligo(ethylene glycol) Diacrylates 189
Anahita Khanlari, Tiffany C. Suekama, Michael S. Detamore, and Stevin H. Gehrke

Author Index 197

Subject Index 199

*Invited Paper

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Hierarchical Self-Assembly of Microgel-Modified Biomaterials Surfaces

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ABSTRACT

Microgels are hydrogel particles with micron and sub-micron diameters. They have been developed, studied, and exploited for a broad range of applications because of their unique combination of size, soft mechanical properties, and controllable network properties. We have been using microgels to modulate the properties of surfaces to differentially control their interactions with tissue cells and bacteria. The long-term goal is to create biomaterials that promote healing while simultaneously inhibiting infection. Because poly(ethylene glycol) [PEG] is used in a number of FDA-approved products and has well-known antifouling properties, we work primarily with PEG-based microgels. We render these anionic either by copolymerization with monomeric acids or by blending with polyacids. Both methods produce pH-dependent negative charge. Surfaces, both planar 2-D surfaces as well as topographically complex 3-D surfaces, can be modified using a hierarchy of non-line-of-sight electrostatic deposition processes that create biomaterials surfaces whose cell adhesiveness is modulated by a sub-monolayer of microgels. Average inter-microgel spacings of 1-2 microns exploit natural differences between staphylococcal bacteria and tissue cells, which open the opportunity to differentially control surface interactions with them based on length-scale effects. After deposition, the microgels can be loaded with a variety of small-molecule, cationic antimicrobials. The details of loading depend on the relative sizes of the antimicrobials and the microgel network structure as well as on the amount and spatial distribution of electrostatic charge within both the microgel and on the antimicrobial. The exposed surface between microgels can be further modified by the adsorption of adhesion-promoting proteins such as fibronectin via electrostatic interaction. This approach combines a rich interplay of microgel structure and chemistry as a key component in a simple and translatable approach to modulate the surface properties of next-generation biomaterials.

INTRODUCTION

Biomaterials-associated infection occurs when bacteria colonize the surface of a tissue-contacting biomedical implant and subsequently infect the surrounding tissue. Such an implant must typically be removed and replaced with significant impact on both the patient and the health-care system. Many strategies are thus being explored to inhibit bacterial colonization of synthetic surfaces. Among them is the creation of antifouling coatings that resist bacterial adhesion [1-10]. In particular, hydrogels and gel-like surfaces have been and continue to be widely studied for use in biomaterials applications because of their ability to control surface interactions with various types of cells.

Among materials used for antifouling applications is poly(ethylene glycol) (PEG). PEG is well known for its resistance to nonspecific protein adsorption and tissue-cell adhesion [11-18]. PEG-based materials also resist bacterial adhesion [3, 9, 10, 19-21]. PEG-based materials

have been used extensively as continuous films or monolayers. We have recently shown that discontinuous PEG coatings are able to resist bacterial adhesion when the length scale of the discontinuities is comparable to that of the bacteria [22]. We used electron-beam lithography to pattern submicron-sized microgels of pure PEG on glass substrates at controlled inter-gel spacings [23], and we found that the adhesion rate of staphylococci, which are spherically shaped and approximately 1 μm in diameter, decreased substantially relative to that on the unpatterned glass control when the inter-gel spacing is 1.5 μm and below [22]. Significantly, however, we found that osteoblast-like cells are still able to adhere to these patterned surfaces despite the non-adhesive microgels [22].

As an alternative to electron-beam patterned microgels, we have also explored creating surfaces with modulated adhesiveness using suspension-polymerized PEG-based microgels deposited by electrostatic self-assembly [24-26]. In contrast to the electron-beam approach, this self-assembly method sacrifices the precise control of both the microgel size and microgel spacing on a surface. Since it is a non-line-of-sight deposition method, however, self-assembly provides the ability to modify complex surfaces such as the roughened implants often used in hip and knee prostheses. Moreover, electrostatic self-assembly is a parallel deposition process that can quickly modify large areas of surface, whereas electron-beam patterning is a serial process better suited for small areas. Suspension polymerization also affords greater flexibility in defining the microgel composition and allows for copolymer synthesis. Much of our current work concentrates, for example, on copolymerizing PEG and acrylic acid (AA). At physiological pH, the deprotonated AA acid groups enhance microgel deposition on poly(L-lysine) primed silicon substrates. While the microgels themselves impart some level of resistance to the adhesion of staphylococcal bacteria [26], this electrostatic charge also allows for the post-deposition loading of microgels by cationic antimicrobial compounds such as peptides and antibiotics.

EXPERIMENTAL APPROACH

We have studied both pure PEG microgels and microgels of PEG containing 10 vol % AA (referred to here as PEG-AA). Prior to use, we typically remove the inhibitor from the commercially purchased poly(ethylene glycol) diacrylate (PEGDA, average M_n 575, Sigma Aldrich) by washing multiple times in hexane. The AA (Acros Organics) can be distilled at 50 °C under reduced pressure. We synthesized microgels from a precursor solution consisting of PEGDA (200 μL), AA (0 or 20 μL), and photoinitiator (10 μL, Darocur 1173, Ciba), all of which were dissolved in dichloromethane (1 mL, DCM, Acros Organics). Deionized water (DI water, 10 mL, Millipore, 18.2 MΩ-cm) was dripped into this precursor solution under constant and rapid stirring until an inverse (DCM in water) emulsion formed. The emulsion was further refined by sonication (Cole-Parmer; 100 W). During sonication the emulsion was exposed to light from a low-pressure ozone-producing ultraviolet (UV) grid lamp for 15 min to drive free-radical polymerization. The resulting microgels were washed in ethanol and DI water and separated by centrifugation. The final suspension was filtered (1.0 μm glass fiber membrane).

Microgels of either PEG or PEG-AA were deposited onto polished Si single-crystal wafer substrates which had been rendered positively charged by priming with poly (L-lysine) [PLL]. After rinsing the as-received wafers in water and in 70% EtOH, the wafers were soaked