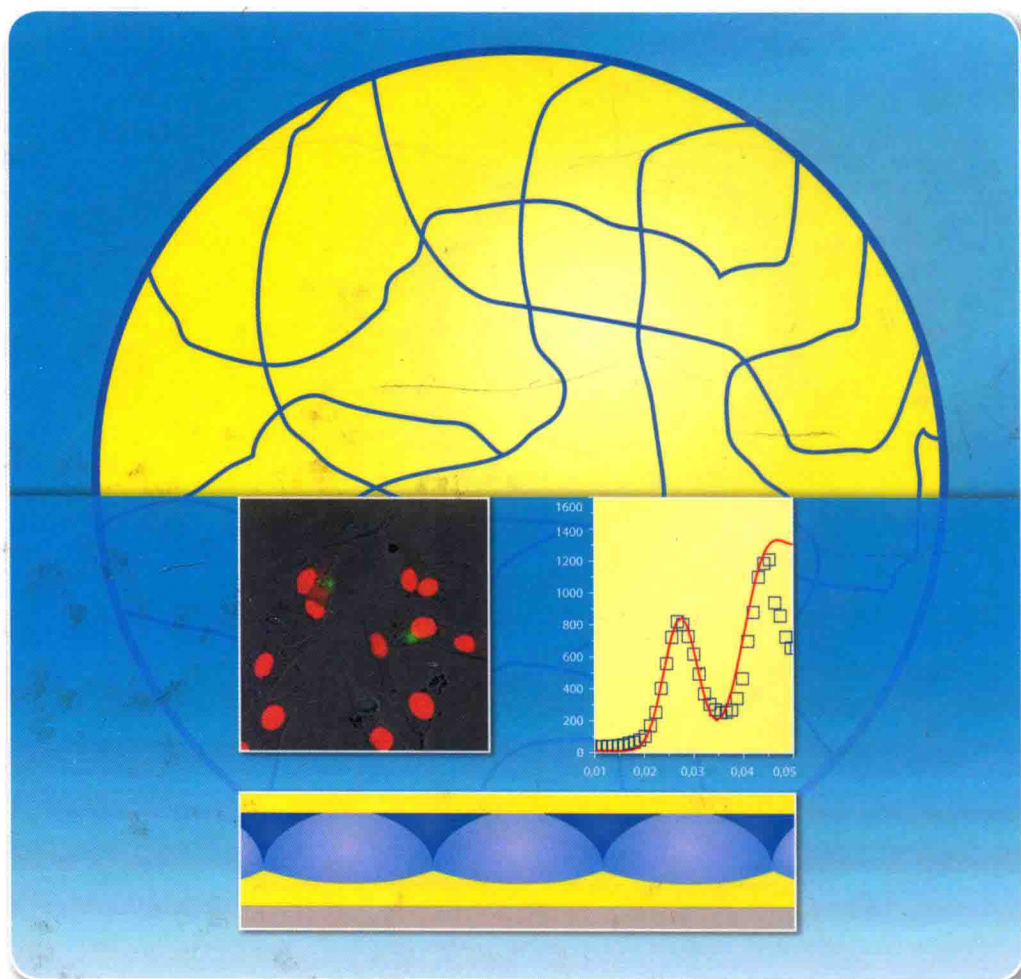


Edited by
L. Andrew Lyon, Michael J. Serpe

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Hydrogel Micro and Nanoparticles



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Foreword

In the unlikely event that you have opened this book without knowing anything about microgels, we start with a definition. Microgels are solvent swollen polymer networks (i.e. a type of gel) present as discrete particles with average diameters in the range 20 nm to 50 μm . Although Baker's first explicit description of microgels in 1949, describes solvent swellable polybutadiene particles, most of the microgel literature concentrates on aqueous microgels (hydrogels) in the size range 100 to 1000 nm. Generalizing more, most of the aqueous microgel publications involve crosslinked poly(N-isopropylacrylamide), PNIPAM, or related polymers showing lower critical solution temperature (LCST) behaviors. Microgel technologies have their roots in latex emulsion polymerization, which is one of the most important historical advances in polymer technology. I mention emulsion polymerization because of the parallels between latex and microgel technologies. Both involve colloidally stable, nano-scale particles with very high specific surface areas and low viscosities. Instrumentation, techniques, and colloidal theories perfected with the advent of monodisperse latexes in the 1960–1980 period are now used to characterize microgels. The ability to apply microelectrophoresis, light scattering, particulate rheology, high performance titrations and small angle neutron scattering to microgel characterization gives researchers a much larger characterization toolbox compared to those working with macrogels.

Microgel research dramatically expanded with the advent of PNIPAM microgels. We made the first PNIPAM microgel in 1978 and we were allowed to publish the work 1986, followed by the first description of a polystyrene-core-PNIPAM shell latex or microgel in 1988 – the definitions blur when considering solid core-gel shell particles. In my opinion, the large number of subsequent microgel publications arises for two reasons. First, microgels based on LCST polymers are extremely easy to make, modify and purify - one does not have to be a highly skilled synthetic polymer chemist to prepare microgels. Second, easy to measure properties including electrophoretic mobility and hydrodynamic particle size from dynamic light scattering, are sensitive functions of temperature, pH, and the presence of surfactants, proteins and other solutes.

The ease of PNIPAM microgel synthesis is a direct consequence of the LCST behavior of PNIPAM. Indeed, I believe that this link to microgel synthesis is the most important consequence of the temperature sensitivity of PNIPAM and related

polymers – there are few applications that actually exploit the temperature sensitivity. The importance of the LCST, or more correctly cloud behavior, in microgel preparation is illustrated by comparing the synthesis of PNIPAM microgels to polyacrylamide microgels. When polymerizing N-isopropylacrylamide in water above the cloud point, the growing polymer chains phase separate (coil-to-globule transition) leading to homogeneous nucleation of dispersed, microgel particles. The PNIPAM particle formation mechanism is analogous to the surfactant-free polymerization of styrene. By contrast, there are very few publications involving cross-linked polyacrylamide microgels because they are difficult to make, and nearly impossible to make as uniform particles. Polyacrylamide is water soluble and does not spontaneously yield microgels. Instead, polyacrylamide microgels must be prepared by a more complex procedure, such as pre-emulsification of aqueous monomer in oil followed by polymerization.

In 2000 I published a review summarizing microgel science and technology – this would be a daunting task now because of the volume of work in the last decade. The ranges of activities summarized in the following chapters highlight the breadth and complexity of the microgel landscape. I finish this essay with my biased view of the main trends in microgel research, and as well, some unanswered questions that have nagged me over the years.

Trend 1 – Applications: In line with the general trends in modern chemistry/material science, microgel publications include a strong emphasis on potential applications. In many cases the potential applications appear to be added as an afterthought, presumably to justify the work; in a few cases the application is the main emphasis and microgels are a means to an end. From my earliest days working with microgels, I have believed there must exist some good applications for microgels. In view of the volume of microgel literature with links to potential applications, many others must feel the same. Some early outstanding examples are Pichot's body of work using microgels as platforms for bioassays, and Asher's concept of responsive microgel-based colloidal arrays. Many clever and more recent examples are found in the following chapters. Nevertheless, one can argue that a "killer application" has yet to surface. To the best of my knowledge, aqueous synthetic microgels are not manufactured in large scale and they do not appear in consumer products. Of course there are food hydrocolloids, nano-particulate starch and other examples of commodities that could be considered as microgels – definitions are always controversial.

Trend 2 – Biodegradable Microgels: I suspect that the largest number of proposed microgel applications is biomedical, and most of those involve controlled drug release. For implanted microgels, biodegradability is an issue. *In vivo* decomposition requires that PNIPAM and other vinyl polymers must be replaced by polyesters, polyamides and other degradable backbones. In many cases biodegradability comes with the cost of losing the exquisite control of composition and particle size achievable with vinyl polymerization.

Trend 3 – Complex Functionalization: The original PNIPAM microgels offered little more than temperature sensitive swelling and a few sulfate or amidine groups. One can find microgel examples of all the popular forms of conjugation from

biotinylation to click chemistry. Because microgels can be dialyzed, filtered, and centrifuged, purification and multi-step reactions are easier with microgels than with the corresponding soluble polymers. In most cases, the starting point for functionalization is the inclusion of carboxyls or amine groups in the parent microgels. With PNIPAM and related microgels, the topochemical distribution of these attachment points within the microgel particles is controlled by the polymerization kinetics.

Trend 4 – Organic/inorganic Composite Microgels: Magnetic microgels, quantum dot-loaded gels, and virtually any other nanoparticle-load microgel one can imagine has been reported. The synthesis either involves growing nanoparticles within the microgels or loading gels with existing particles. These systems should greatly expand the application space for microgels. Hellweg in Chapter 2 describes examples of composite microgels.

Trend 5 – Assembled Microgels: In my view, one of the most promising areas for microgels involves the assembly of microgels in much larger and complex structures. The early papers by Sandy Asher, Zhibing Hu and Andrew Lyon focused on exploiting the environmentally sensitive photonic properties of microgel based colloidal crystals. Microgels are readily printed by ink jet and other water-based printing technologies, facilitating roll-to-roll manufacturing of patterned surfaces. Surely the “killer application” is coming.

Microgel science is mature. With a thirty plus year history and the accumulated knowledge in hundreds of publications, it is possible to synthesize and characterize almost any microgel structure one could imagine. Nevertheless, there are some gaps. With the exception of neutron scattering, there are few (no?) tools to measure the mass and functional group distribution within microgel particles. Compared to our structural knowledge of proteins such as enzymes or other synthetic systems such as self-assembled monolayers, we know little about the detailed organization of microgels. Controlled radical polymerizations should give better control of microgel structure, facilitating characterization – see Matyjaszewski, Chapter 9.

The polymer reaction engineering aspects of microgels have received little attention. Hoare’s work is the only significant kinetic modeling and there have been few measurements of microgel polymerization kinetics. Such work will be required to transform impractical academic microgel recipes (dilute solution, long reaction times, and purification by ultracentrifugation) into a commercial process when large scale applications emerge.

In closing, microgels are an established subset of the materials toolbox. The chapters herein describe fascinating phenomena that point to a multitude of potential applications. In my view, microgel science will not evolve as a separate field but will continue to occupy an important position in the hierarchy of nano-colloidal dispersed systems.

Robert Pelton
McMaster University

Preface

The idea of polymers, or more colloquially “plastics”, was initially met with scrutiny at the time of the initial experiments of Staudinger and Carothers. Despite this scrutiny, their ideas were eventually accepted, and these days one would be hard pressed to live one day (possibly one minute) without having contact with polymer-based materials. Whereas countless varieties of polymers, and polymer-based materials exist, this book focuses solely on colloidally stable hydrogel particles. Hydrogel particles, often referred to as microgels or nanogels depending on the length scale of their smallest dimension, are composed of a cross-linked hydrophilic polymer network. Because of the hydrophilicity of the polymer, and the cross-linked nature of the structure, the particles swell with water, typically taking on a spherical shape. Hydrogel particles have found their way into numerous applications ranging from lubricants in machinery to targeted/controlled drug delivery. Looking forward, there are still many potential applications that could benefit tremendously from new, enabling microgel-based materials. With the prospect of revolutionizing specific technologies, comes basic research; this book is meant to highlight the most exciting and impactful current research in the fields of microgels and nanogels. The volume was assembled to highlight the newest synthetic routes, characterization methods, and applications emergent in the area. Leaders in the field have contributed chapters representative of their most recent results from their respective labs, thereby shedding light on the enormous potential of this unique class of matter.

In editing this book the authors owe a great deal of thanks to our respective group members for volunteering their time to aid with the review process of the submitted chapters. We also owe a great deal of gratitude to Anja Tschörtlner and Martin Preuss of Wiley for allowing us the opportunity to edit this volume, and for their assistance along the way.

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