Polyelectrolyte hydrogels

Last Day: Physical hydrogels
Structure and physical chemistry

Today: polyelectrolyte hydrogels, complexes, and coacervates
Polyelectrolyte multilayers
theory of swelling in ionic hydrogels


Supplementary Reading:

ANNOUNCEMENTS:
Determination of thermodynamic driving force for triblock self-assembly

Image removed due to copyright reasons.

Please see:
Figure 6 and Table 4 in Alexandridis, P., J. F. Holzwarth, and T. A. Hatton. Macromolecules 27 (1994): 2414-2425.
Determination of thermodynamic driving force for triblock self-assembly
Hydrophobic association vs. hydrogen bonding gels
Polyelectrolyte hydrogels
Common polyelectrolyte gel structures:
Formation of polyelectrolyte physical gels: self-assembly of coacervate hydrogels

Images removed due to copyright reasons:
Please see:
Microstructure of coacervate hydrogels

Xanthan polyanion

Chitosan polycation

Images removed due to copyright reasons.
Please see:
Microstructure of coacervate hydrogels

Images removed due to copyright reasons.

Please see:

Images removed due to copyright reasons.

Please see:
Layer-by-layer deposition

Image removed due to copyright reasons:
Please see:

Figure 1 in Schlenoff, Joseph B. "Polyelectrolyte Multilayers." AccessScience@McGraw-Hill.
http://www.accessscience.com

Figure by MIT OCW.

Advancing contact angle as a function of the layer number of PSS and chitosan. Odd numbers represent films with PSS as the outermost layer, whereas even number films have chitosan as the outermost layer.
Degree of ionization during assembly dictates multilayer structure

Charge during assembly can be ‘protected’ in the multilayer:

Images removed due to copyright reasons.
Please see:
Assembly with any charged molecule or particle; Conformal modification of complex surfaces

Images removed due to copyright reasons.

Please see:
Conformal modification of complex surfaces

Image removed due to copyright reasons.

Please see:
Hollow PEMs as drug-delivery capsules

Fluorescent drug-loaded PEM capsules
Cellular substrates

Image of SEM micrograph of multilayer-coated echinocyte blood cell removed due to copyright restrictions.

(Alberts et al. Molecular Biology of the Cell)
Employing PEMs on degradable biomaterials

Images removed due to copyright reasons.
Please see:
Polyelectrolyte hydrogels

\[ K_a = \frac{[\text{RCOO}^-][\text{H}^+]}{[\text{RCOOH}]} \]

\[ pK_a = -\log K_a \]

\[ \text{pH} = pK_a + \log \frac{[\text{RCOO}^-]}{[\text{RCOOH}]} \]
Responsiveness of ‘unpaired’ polyelectrolyte gel structures:

- pH
- Ionic strength
- Electric fields
- (temperature)

E
Environmental responsiveness of covalent polyelectrolyte networks: experimentally observed swelling of anionic hydrogels

Driving force for unpaired polyelectrolyte gel swelling

\[ \text{COO}^- \quad \text{H}^+ \quad \text{H}_2\text{O} \quad \text{OH}^- \]

(1)

\[ \text{Na}^+ \quad \text{Cl}^- \quad \text{OH}^- \quad \text{Na}^+ \]

(2)

\[ \Pi \]

(3)

(4)
Swelling behavior reversed in polycation hydrogels
Kinetics of swelling/deswelling transitions

Graphs removed due to copyright reasons.
Please see:
Kinetics of swelling/deswelling transitions

Rapid swelling/deswelling of superporous gels:

Low pH

High pH

Graph removed due to copyright reasons. Please see: Figure 2 in Zhao, B., and J. S. Moore. “Fast pH- and Ionic Strength-responsive Hydrogels in Microchannels.” *Langmuir* 17(2001): 4758-4763.
thermodynamics of ionic hydrogels

Model of system:

- Inorganic anion, e.g. Cl⁻
- Inorganic cation, e.g. Na⁺
- Water
Swelling of polyelectrolyte gels is controlled by ionic strength and degree of ionization of the gel:
Equilibrium condition:
\[ Q = \text{swollen volume of system/dry polymer volume} = \frac{1}{\phi_{2,s}} \]

Theoretical Swelling Predictions at Comparable Ionic Strength Conditions for an Anionic Network

PE hydrogels as environment-responsive materials: applications in biotechnology and bioengineering
bioMEMS based on polyelektrolyte gel responses

Images removed due to copyright reasons. Please see:
Figure 1 and Figure 2 in Beebe, D. J., et al. “Functional Hydrogel Structures for Autonomous Flow Control Inside Microfluidic Channels.” Nature 404 (2000): 588-+.
bioMEMS based on polyelectrolyte gel responses


Further Reading