Polyelectrolyte hydrogels

Last Day:	Physical hydrogels Structure and physical chemistry
Today:	polyelectrolyte hydrogels, complexes, and coacervates Polyelectrolyte multilayers theory of swelling in ionic hydrogels
Reading:	S.K. De et al., 'Equilibrium swelling and kinetics of pH-responsive hydrogels: Models, experiments, and simulations,' *J. Microelectromech. Sys*. **11**(5) 544 (2002).
Supplementary Reading:	

ANNOUNCEMENTS:

Determination of thermodynamic driving force for triblock self-assembly

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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:

COACERVATES

Formation of polyelectrolyte physical gels: self-assembly of coacervate hydrogels

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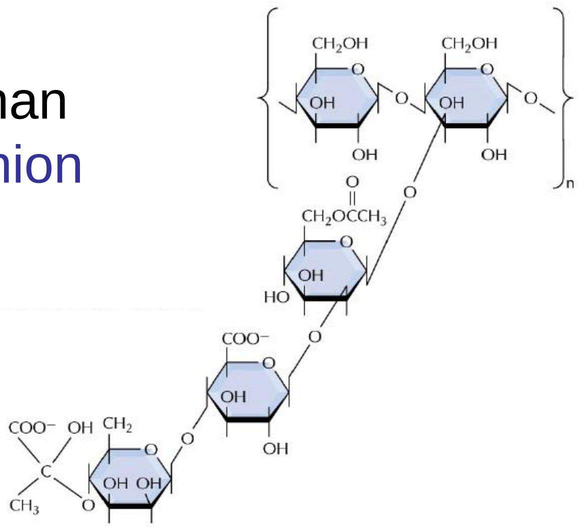
Please see:

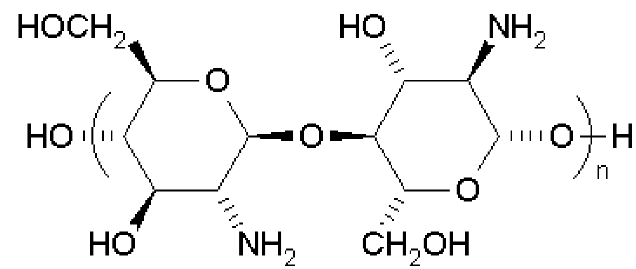
Chornet, E., and S. Dumitriu. "Inclusion and Release of Proteins from Polysaccharide-based Polyion Complexes." *Adv Drug Deliv Rev* 31 (1998): 223-246.

Microstructure of coacervate hydrogels

Xanthan
polyanion



Chitosan
polycation



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Please see:
Chornet, E., and S. Dumitriu. “Inclusion and Release of Proteins from Polysaccharide-based Polyion Complexes.” *Adv Drug Deliv Rev* 31 (1998): 223-246.

COACERVATES

Microstructure of coacervate hydrogels

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Please see:
Chornet, E., and S. Dumitriu. “Inclusion and Release of Proteins from Polysaccharide-based Polyion Complexes.” *Adv Drug Deliv Rev* 31(1998): 223-246.

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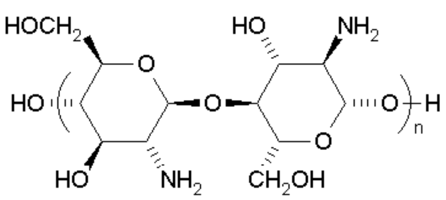
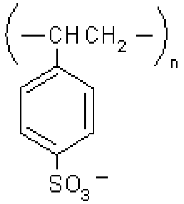
Please see:
Friedl, P. et al. *Eur J. Immunol* 28 (1998): 2331-2343.

Layer-by-layer deposition





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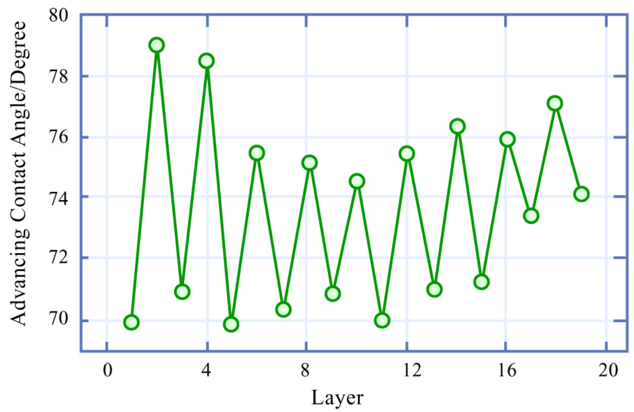
Please see:

Figure 1 in Schlenoff, Joseph B. "Polyelectrolyte Multilayers.“ AccessScience@McGraw-Hill.

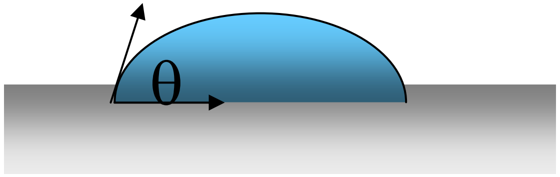
http://www.accessscience.com

Surface properties dominated by last layer deposited:



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.

Figure by MIT OCW.



PEMs

Degree of ionization during assembly dictates multilayer structure

Charge during assembly can be 'protected' in the multilayer:

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Please see:
Figure 1 in Mendelsohn, Jonas D., Sung Yun Yang, Jeri'Ann Hiller, Allon I. Hochbaum, and Michael F. Rubner. "Rational Design of Cytophilic and Cytophobic Polyelectrolyte Multilayer Thin Films." *Biomacromolecules* 4 (2003): 96-106.

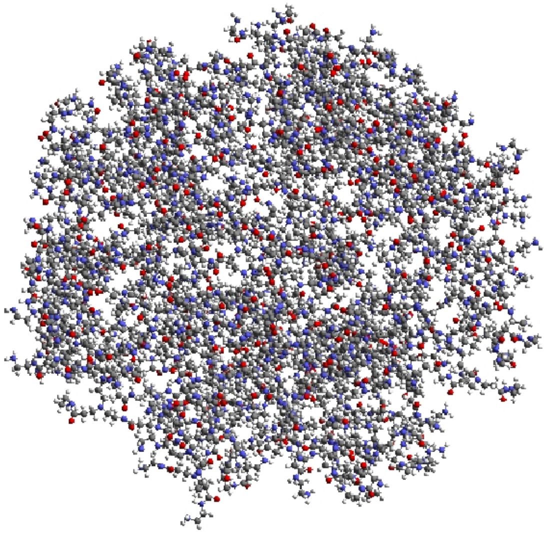
PEMs

Assembly with any charged molecule or particle; Conformal modification of complex surfaces

Images removed due to copyright reasons.

Please see:

Khopade, A. J., and F. Caruso. “Stepwise Self-assembled Poly(amidoamine) Dendrimer and Poly(styrenesulfonate) Microcapsules as Sustained Delivery Vehicles.” *Biomacromolecules* 3 (2002): 1154-1162.



Conformal modification of complex surfaces

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Please see:
Caruso, F., D. Trau, H. Mohwald, and R. Renneberg. "Enzyme Encapsulation in Layer-by-layer Engineered Polymer multilayer capsules." *Langmuir* 16 (2000): 1485-1488.

Hollow PEMs as drug-delivery capsules

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Graph removed due to copyright restrictions.

Fluorescent drug-loaded PEM capsules

Cellular substrates

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

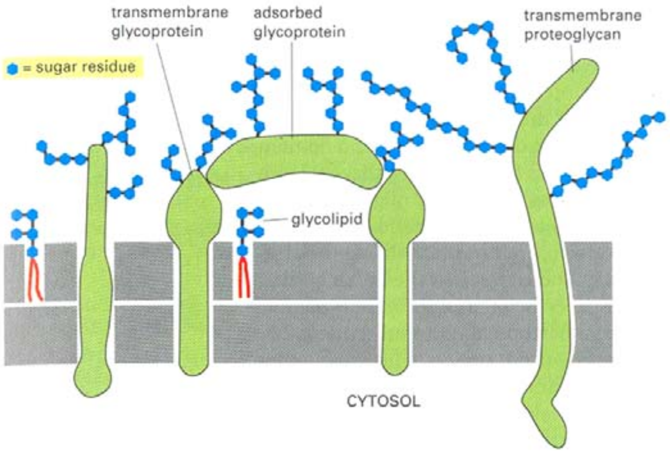
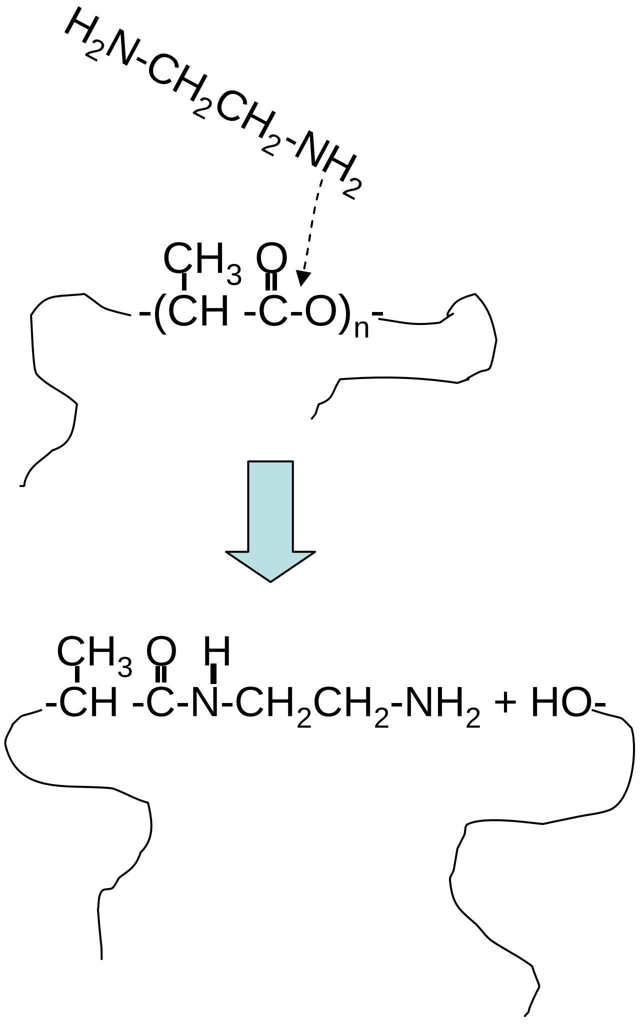


Figure 10–41 Simplified diagram of the cell coat (glycocalyx). The cell coat is made up of the oligosaccharide side chains of glycolipids and integral membrane glycoproteins and the polysaccharide chains on integral membrane proteoglycans. In addition, adsorbed glycoproteins and adsorbed proteoglycans (not shown) contribute to the glycocalyx in many cells. Note that all of the carbohydrate is on the noncytoplasmic surface of the membrane.

(Alberts et al. *Molecular Biology of the Cell*)

Employing PEMs on degradable biomaterials



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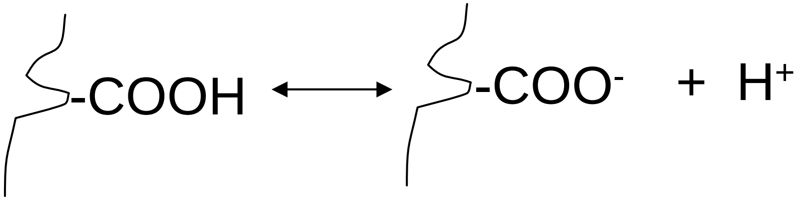
Please see:
Zhu, Y., C. Gao, T. He, X. Liu, and J. Shen. "Layer-by-Layer Assembly to Modify Poly(L-lactic acid) Surface Toward Improving Its Cytocompatibility to Human Endothelial Cells." *Biomacromol.* 4 (2003): 446-452.

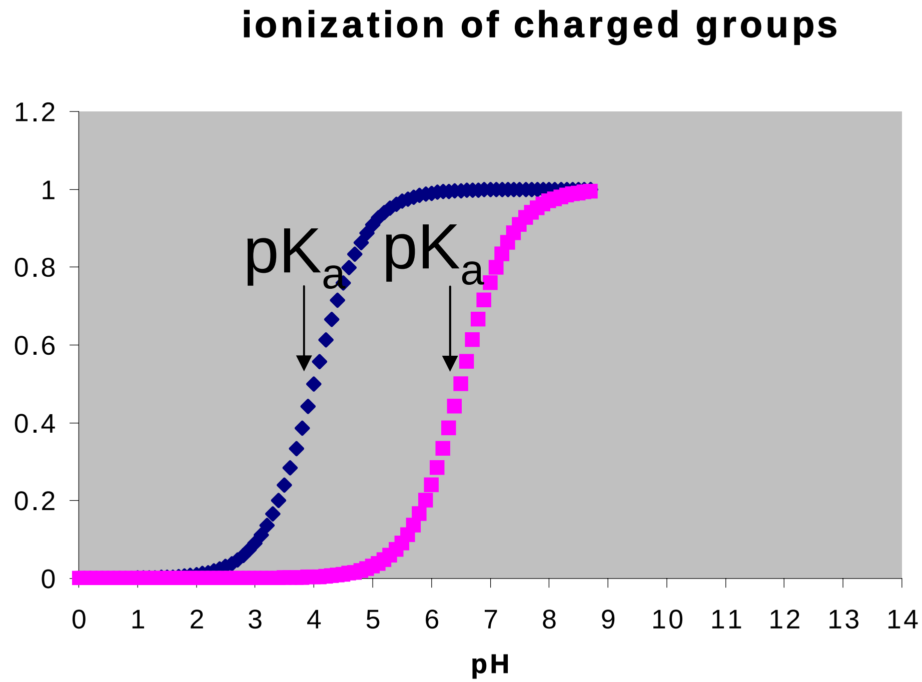
Polyelectrolyte hydrogels



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

$$pK_a = -\log K_a$$

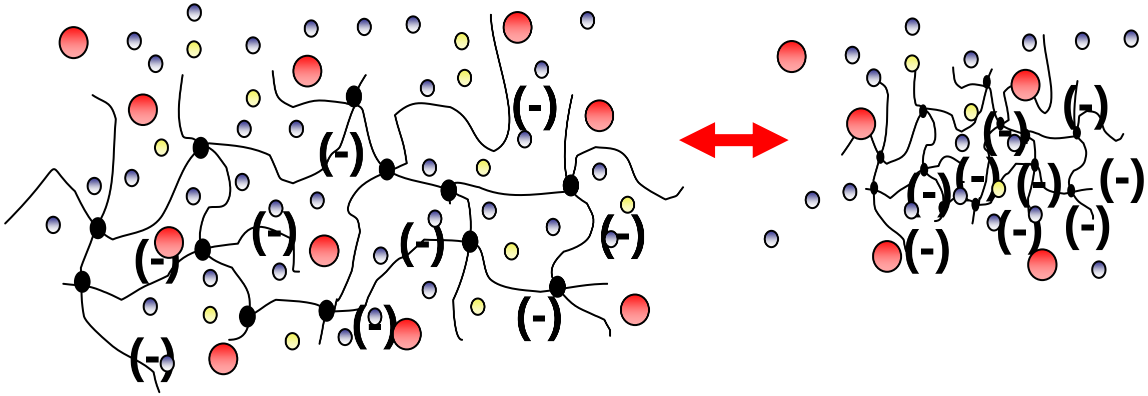
$$pH = pK_a + \log [RCOO^-]/[RCOOH]$$



Responsiveness of ‘unpaired’ polyelectrolyte gel structures:

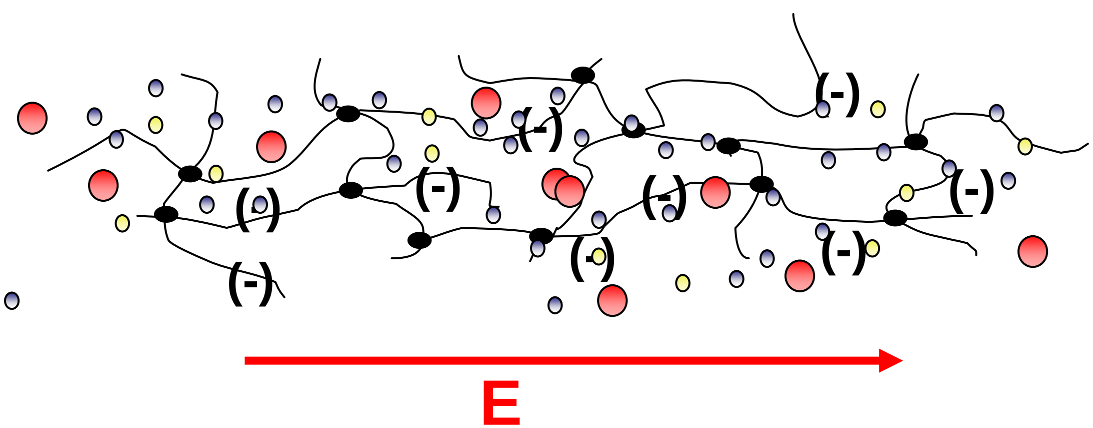
pH

Ionic strength

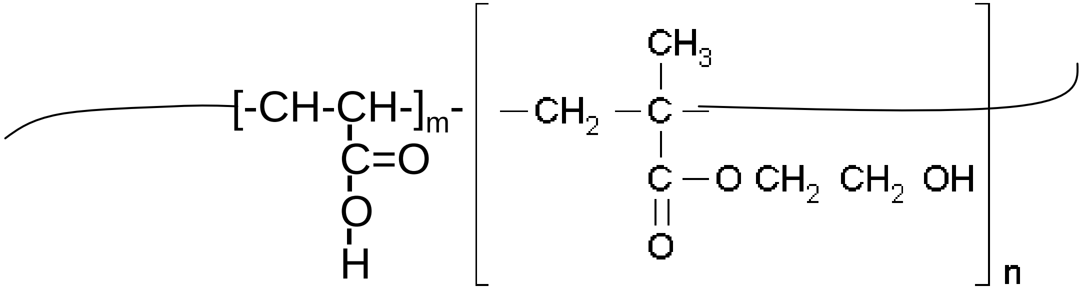


Electric fields

(temperature)



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



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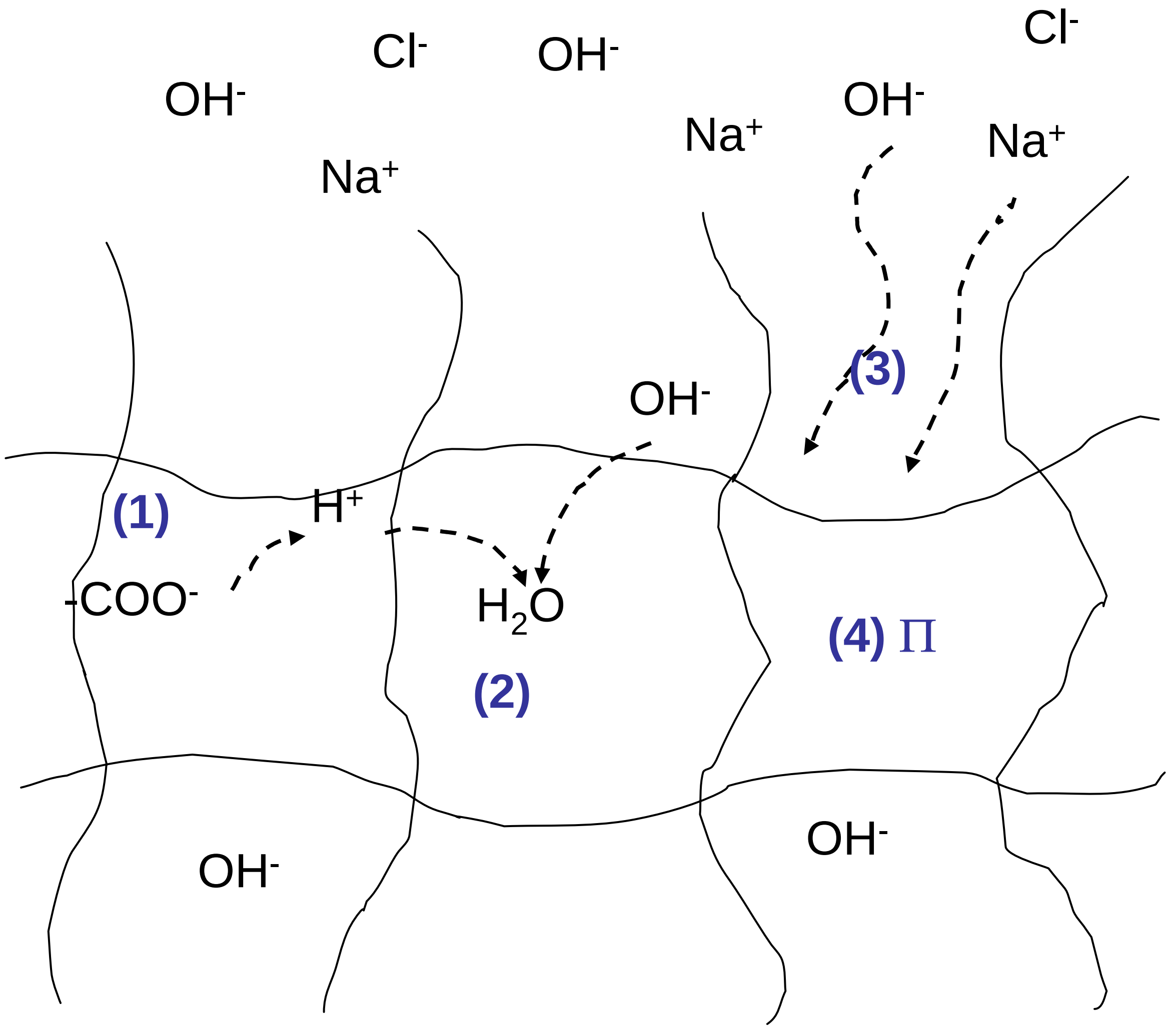
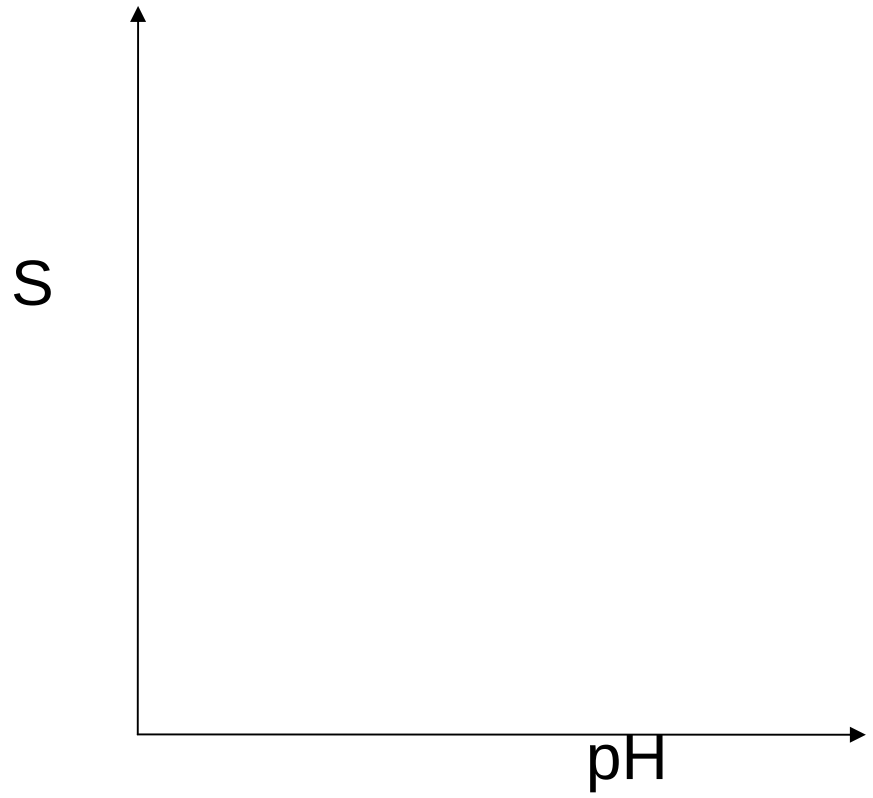
Please see:
De, S. K. et al. “Equilibrium Swelling and Kinetics of pH-responsive Hydrogels: Models, Experiments, and Simulations.” *Journal of Microelectromechanical Systems* 11 (2002): 544-555.

Driving force for unpaired polyelectrolyte gel swelling



Swelling behavior reversed in polycation hydrogels



Kinetics of swelling/deswelling transitions

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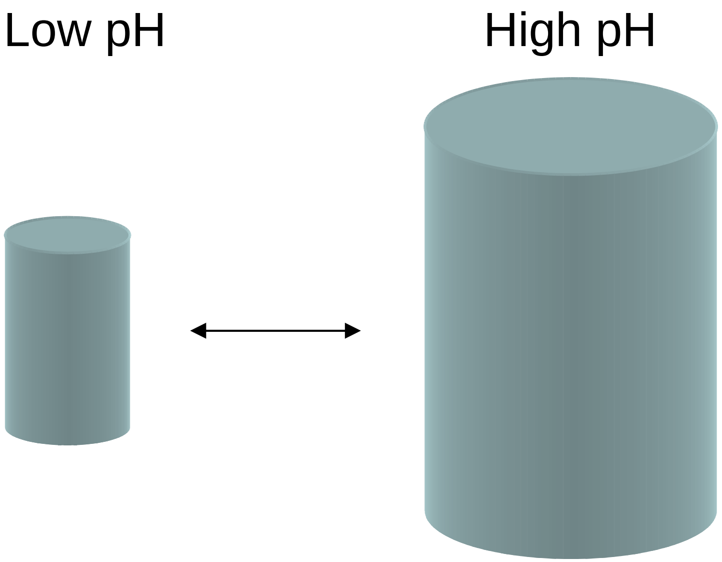
Please see:
De, S. K. et al. "Equilibrium Swelling and Kinetics of pH-responsive Hydrogels: Models, Experiments, and Simulations." *Journal of Microelectromechanical Systems* 11 (2002): 544-555.

Kinetics of swelling/deswelling transitions

Rapid swelling/deswelling of superporous gels:



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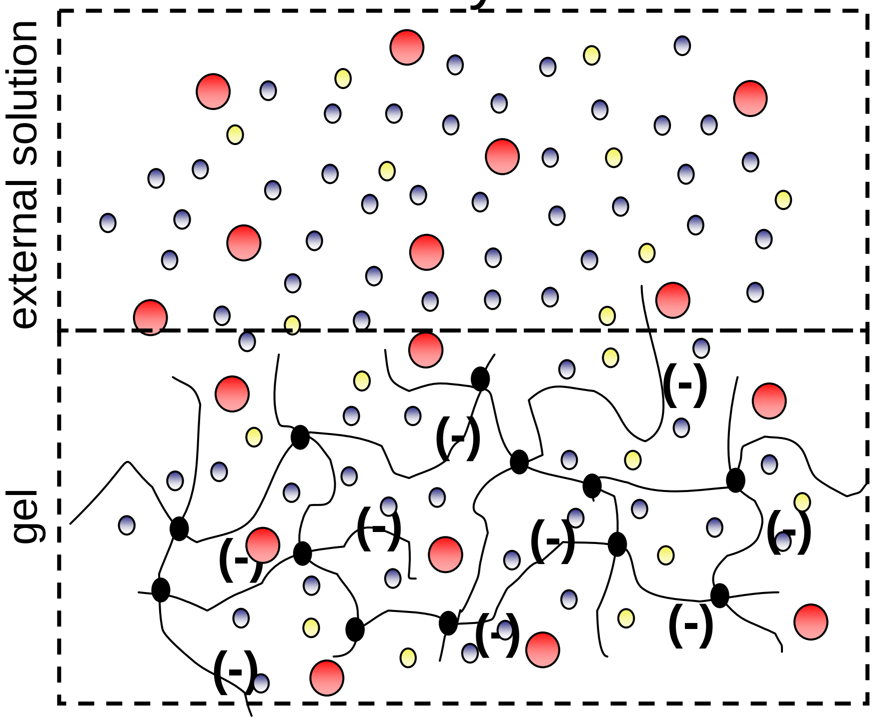
Please see:
Figure 2 in Zhao, B., and J. S. Moore. "Fast pH- and Ionic Strength-responsive Hydrogels in Microchannels." *Langmuir* 17(2001): 4758-4763.

thermodynamics of ionic hydrogels

Model of system:



Inorganic anion, e.g. Cl^-

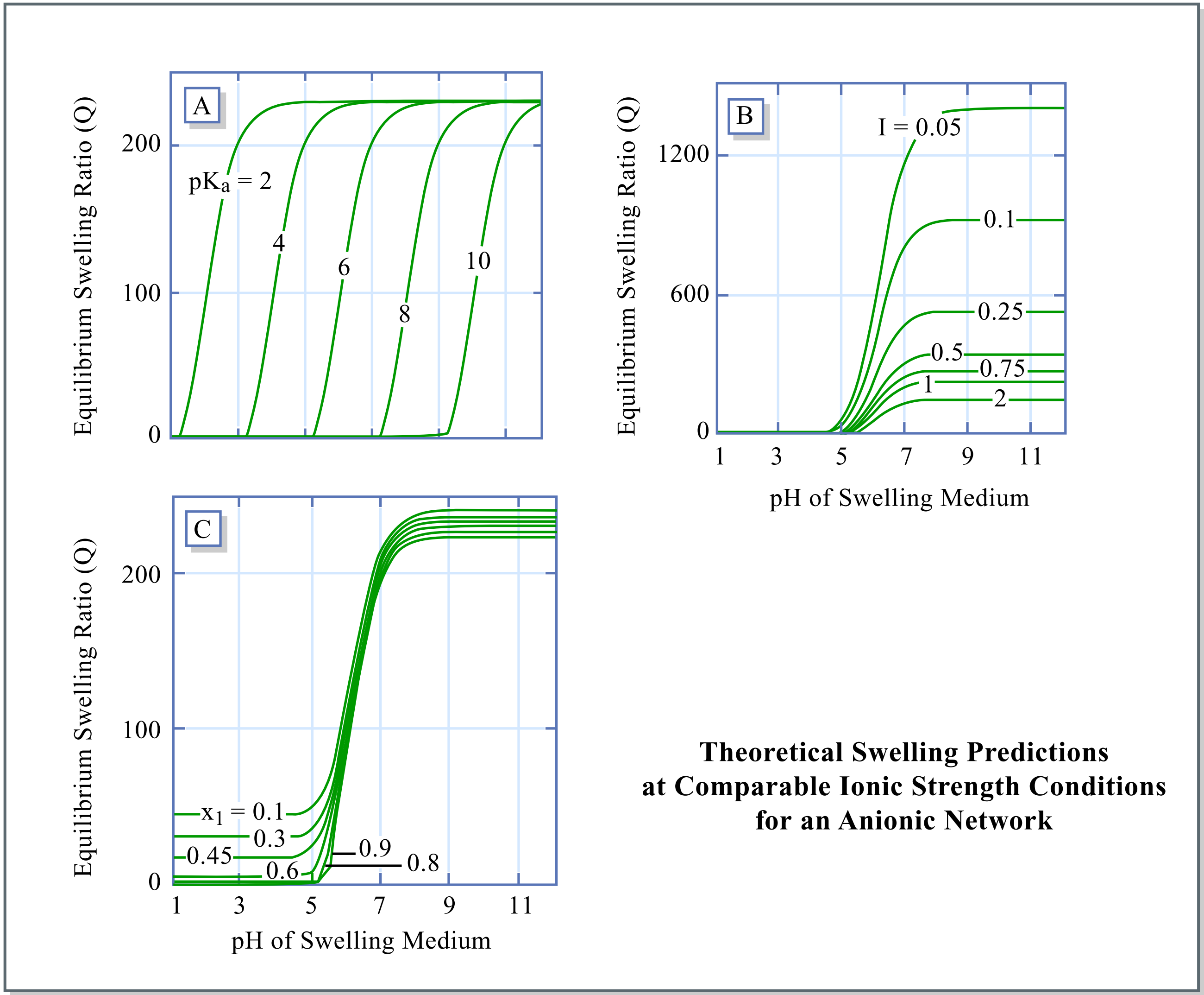
Inorganic cation, e.g. Na^+

water

Swelling of polyelectrolyte gels is controlled by ionic strength and degree of ionization of the gel:

Equilibrium condition:

Q = swollen volume of system/dry polymer volume $= 1/\phi_{2,s}$



After Brannonpeppas, L., and N. A. Peppas. "Equilibrium Swelling Behavior of Ph-Sensitive Hydrogels." *Chemical Engineering Science* 46 (1991): 715-722.

Figure by MIT OCW.

PE hydrogels as environment-responsive materials: applications in biotechnology and bioengineering

bioMEMS based on polyeletrolyte gel responses

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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 polyeletrolyte gel responses

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Please see:
Figure 12 in Beebe, D. J., G. A. Mensing, and G. M. Walker. "Physics and Applications of Microfluidics in Biology." *Annual Review of Biomedical Engineering* 4 (2002): 261-286.

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Please see:
Figure 4 in Beebe, D. J., et al. "Functional Hydrogel Structures for Autonomous Flow Control Inside Microfluidic Channels." *Nature* 404 (2000): 588-+.

Further Reading

1. De, S. K. et al. Equilibrium swelling and kinetics of pH-responsive hydrogels: Models, experiments, and simulations. *Journal of Microelectromechanical Systems* **11**, 544-555 (2002).
2. Tanaka, T. & Fillmore, D. J. Kinetics of Swelling of Gels. *Journal of Chemical Physics* **70**, 1214-1218 (1979).
3. Zhao, B. & Moore, J. S. Fast pH- and ionic strength-responsive hydrogels in microchannels. *Langmuir* **17**, 4758-4763 (2001).
4. Chornet, E. & Dumitriu, S. Inclusion and release of proteins from polysaccharide-based polyion complexes. *Adv Drug Deliv Rev* **31**, 223-246. (1998).
5. Zhu, Y., Gao, C., He, T., Liu, X. & Shen, J. Layer-by-Layer assembly to modify poly(L-lactic acid) surface toward improving its cytocompatibility to human endothelial cells. *Biomacromol.* **4**, 446-452 (2003).
6. Khopade, A. J. & Caruso, F. Stepwise self-assembled poly(amidoamine) dendrimer and poly(styrenesulfonate) microcapsules as sustained delivery vehicles. *Biomacromolecules* **3**, 1154-1162 (2002).
7. Caruso, F., Trau, D., Mohwald, H. & Renneberg, R. Enzyme encapsulation in layer-by-layer engineered polymer multilayer capsules. *Langmuir* **16**, 1485-1488 (2000).
8. Elbert, D. L., Herbert, C. B. & Hubbell, J. A. Thin polymer layers formed by polyelectrolyte multilayer techniques on biological surfaces. *Langmuir* **15**, 5355-5362 (1999).
9. Wang, Y. F., Gao, J. Y. & Dubin, P. L. Protein separation via polyelectrolyte coacervation: Selectivity and efficiency. *Biotechnology Progress* **12**, 356-362 (1996).
10. Beebe, D. J. et al. Functional hydrogel structures for autonomous flow control inside microfluidic channels. *Nature* **404**, 588-+ (2000).
11. Beebe, D. J., Mensing, G. A. & Walker, G. M. Physics and applications of microfluidics in biology. *Annual Review of Biomedical Engineering* **4**, 261-286 (2002).
12. James, H. M. & Guth, E. Simple presentation of network theory of rubber, with a discussion of other theories. *J. Polym. Sci.* **4**, 153-182 (1949).
13. Flory, P. J. & Rehner Jr., J. Statistical mechanics of cross-linked polymer networks. I. Rubberlike elasticity. *J. Chem. Phys.* **11**, 512-520 (1943).
14. Flory, P. J. & Rehner Jr., J. Statistical mechanics of cross-linked polymer networks. II. Swelling. *J. Chem. Phys.* **11**, 521-526 (1943).
15. Brannonpeppas, L. & Peppas, N. A. Equilibrium Swelling Behavior of Ph-Sensitive Hydrogels. *Chemical Engineering Science* **46**, 715-722 (1991).
16. Peppas, N. A. & Merrill, E. W. Polyvinyl-Alcohol) Hydrogels - Reinforcement of Radiation-Crosslinked Networks by Crystallization. *Journal of Polymer Science Part a-Polymer Chemistry* **14**, 441-457 (1976).
17. Ozyurek, C., Caykara, T., Kantoglu, O. & Guven, O. Characterization of network structure of poly(N-vinyl 2-pyrrolidone/acrylic acid) polyelectrolyte hydrogels by swelling measurements. *Journal of Polymer Science Part B-Polymer Physics* **38**, 3309-3317 (2000).