Karlsruher Institut für Technologie

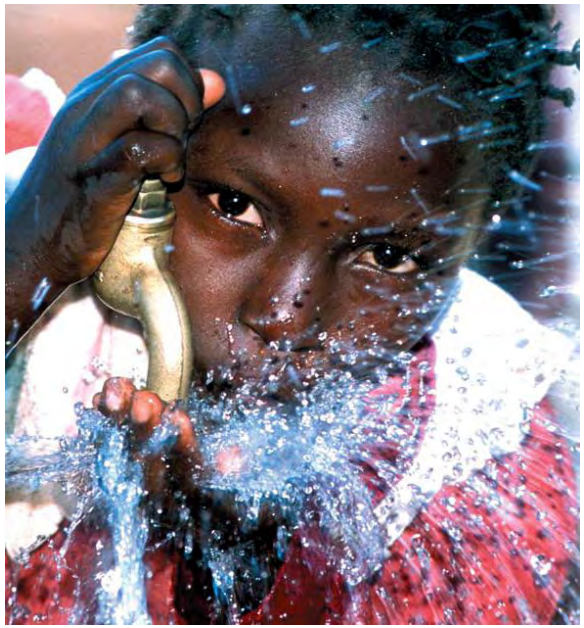
Synthesis and Characterization of Sulfonated Polystyrene Networks for the Desalination of Seawater

Christoph Pfeifer, **Garching 17.06.2016**

Sonderforschungsbereich 1176

Motivation

- in 2005 about 1.1 billion people in the world face insufficient supply of drinking water [1]
- desalination of seawater an appropriate tool to overcome this malnutrition



[1]

- first desalination approaches based on polyacrylate networks
- possible alternative: polystyrene sulfonate

[1] WHO, UNICEF, *Joint Monitoring Program for Water Supply and Sanitation. Water for life : making it happen.*, 1 ed., WHO Press, Genf, **2005**.

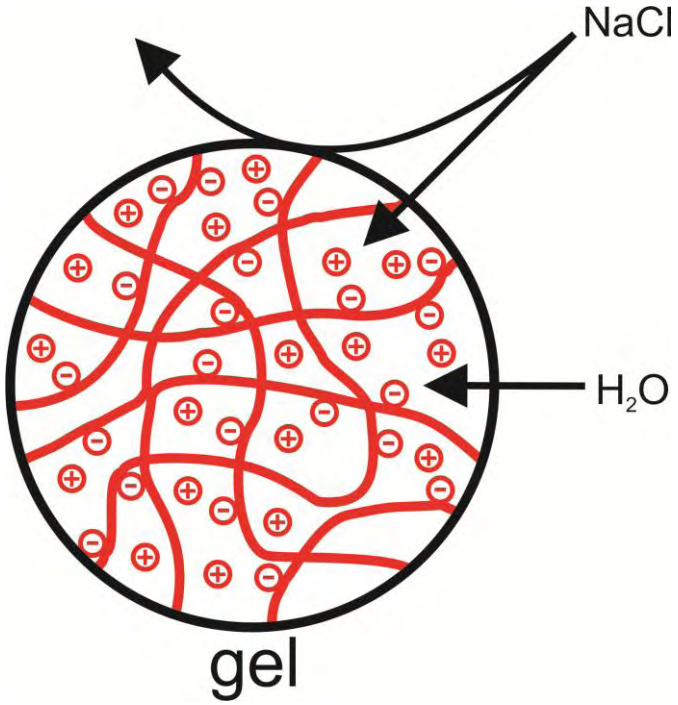
Theory

- water enters polyelectrolyte (osmotic pressure)
- ions are repelled by polyelectrolyte (Coulomb)
- swelling behavior of polyelectrolytes described by modified Flory-Rehner theory:

[2]

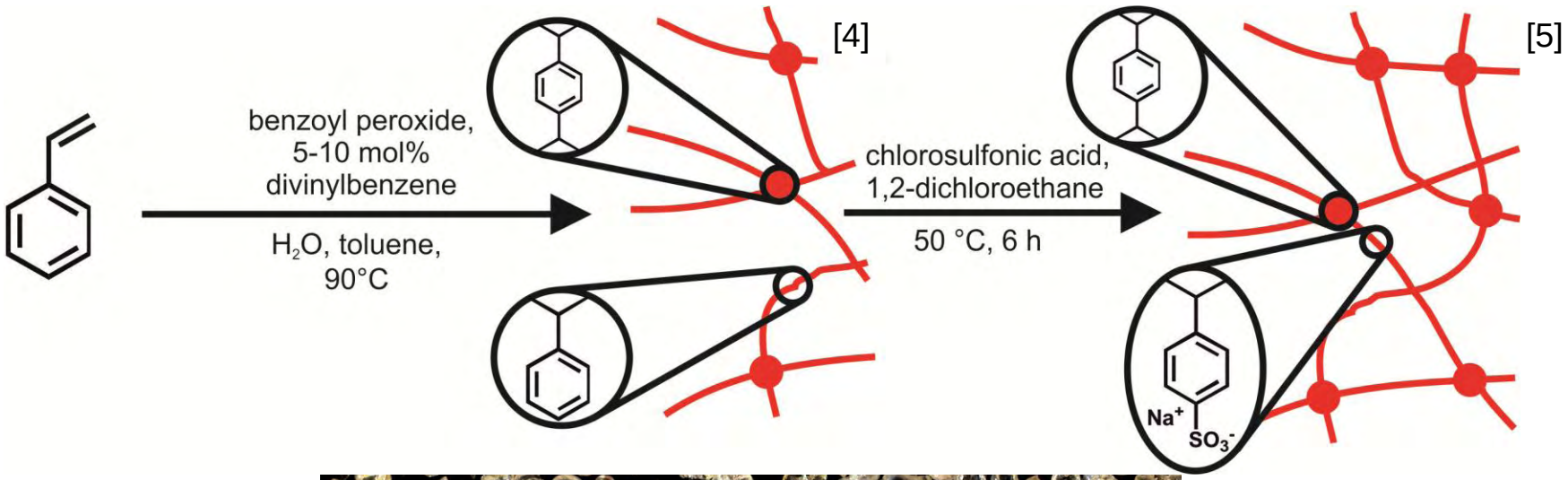
$$\tilde{U}^{\frac{3}{1}} \text{ سي طي} \left[\left(\frac{\ddot{\Omega}}{\varsigma \dot{\omega} \sqrt{\ddot{\Omega}}} \right) \cdot \text{ ط} \frac{(\rho \, j \, \varsigma \text{ طي } ?_{o})}{\dot{\omega}_{\text{ظ}}} \right] \frac{\dot{\omega}_{\text{ي}}}{\text{Ч}_{\text{ز}}} \quad [3]$$

i/V_u concentration of fixed charges in the unswollen polymer, I ionic strength in solution, χ_1 Flory-Huggins parameter, V_1 molar volume of the solvent, ν_e/V_0 cross-linking density



[2] http://www.sagisa.com/dow/DOWEX-Ion-Exchange-Resins.php (Stand: 08.07.15)
[3] Flory, Paul. Principles of polymer chemistry. Cornell Univ. Pr., 1953.

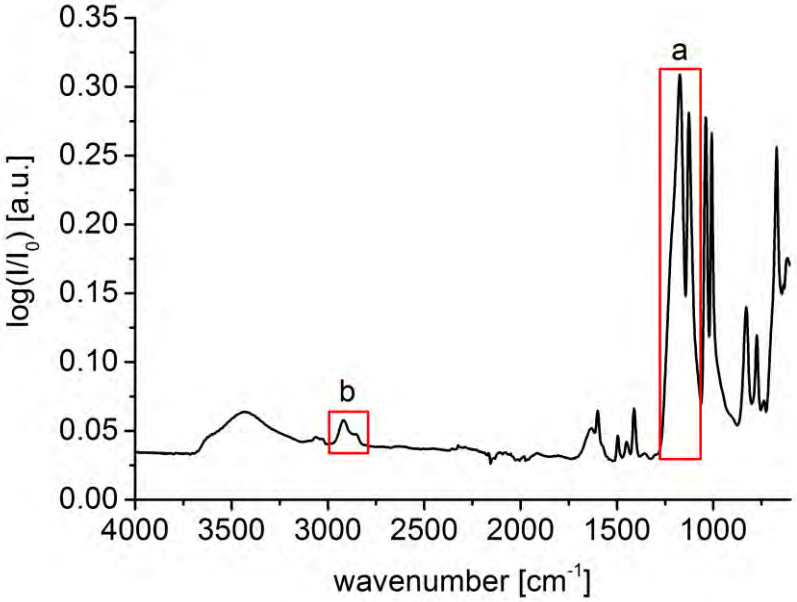
Synthesis



[4] Abere, J., Goldfinger, G., Naidus, H., & Mark, H. (1944). Polymerisation of Styrene Under Various Experiamental Conditions, *1*(15).
[5] Gupta, B., Büchi, F. N. (1996). Crosslinked ion exchange membranes by radiation grafting of styrene/divinylbenzene into FEP films. *Journal of Membrane Science*, *118*, 231–238.

Degree of Sulfonation

infrared (IR) spectrum of polystyrene sulfonate



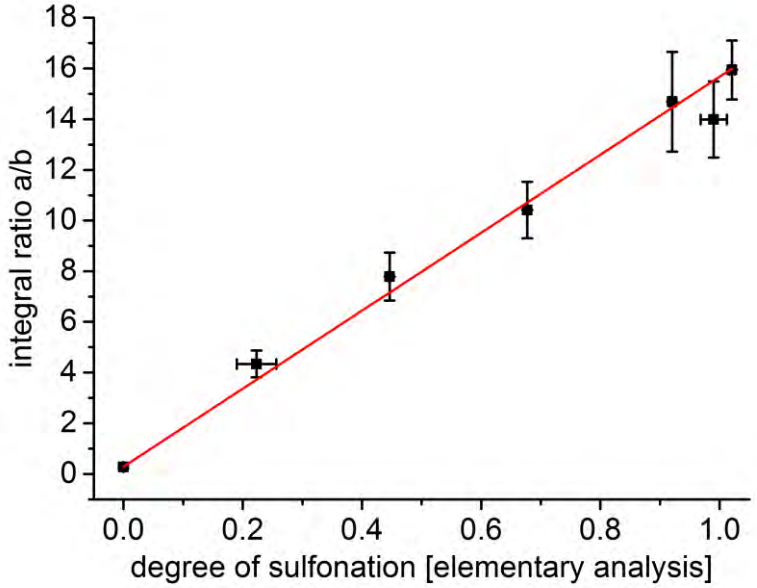
- determined by IR spectroscopy and elementary analysis
- peak a – sulfonate group (S=O stretch vibration)
- peak b – polymer backbone (C-H stretch vibration)

- average of 5 measurements
- ratio a/b linear
- good agreement with Lambert-Beer

$$\frac{I}{I_0} = e^{-\varepsilon \cdot c \cdot d}$$

I/I_0 normalized intensity, c concentration, ε extinction coefficient, d distance

comparison peak ratio a/b to elementary analysis



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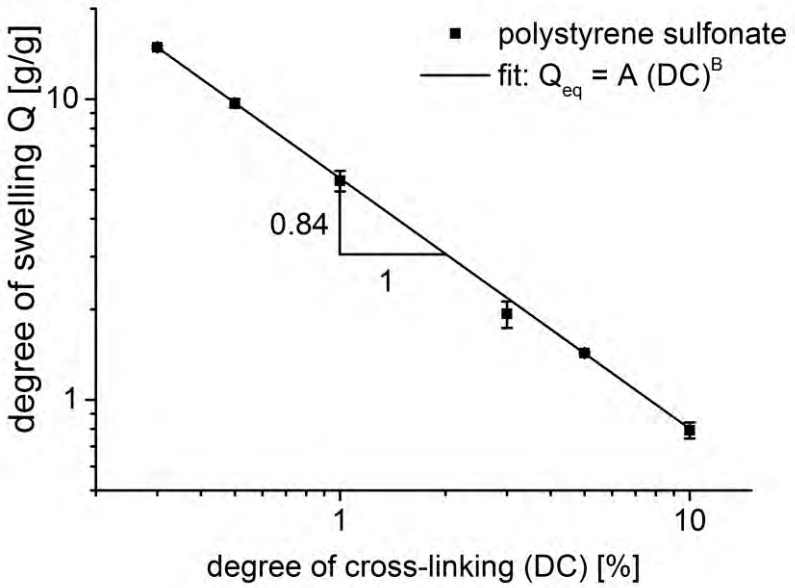
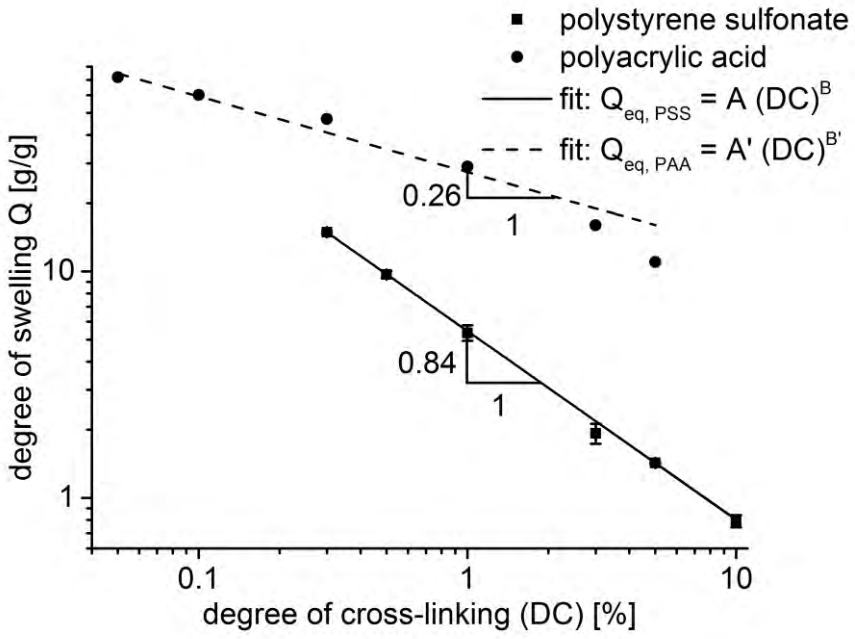
Swelling Experiments



- sulfonated polystyrene swollen with 1 wt.% NaCl solution
- degree of swelling $Q = m_{water}/m_{polymer}$
- slope B of 0.84 showed decent agreement with Flory-Rehner theory

- lower degrees of swelling than polyacrylic acid
- higher dependency on degree of cross-linking



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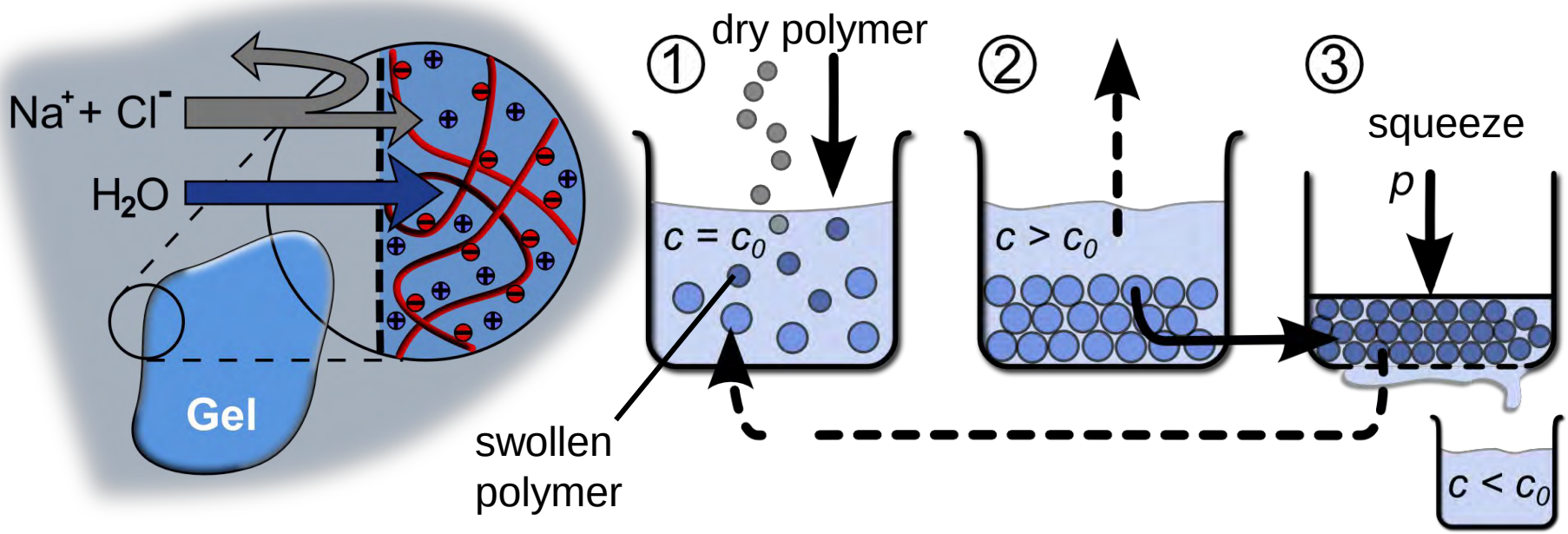
Desalination – Hydrogel Process

- absorption of large amounts of aqueous solution in hydrogel, e.g. polystyrene sulfonate PSS
- external electrolyte is repelled by the charged polymer
- realization in a 3-step process



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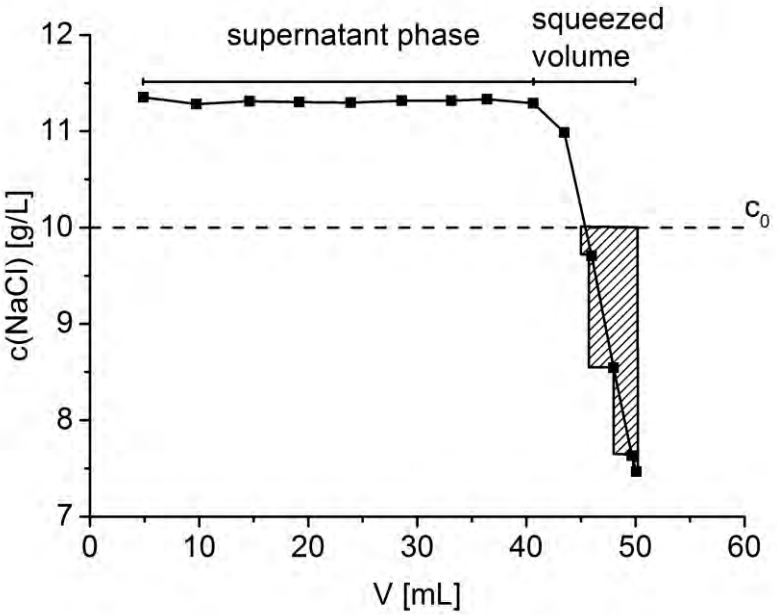
Desalination – Idealized Run

salt concentration vs. squeezed volume during desalination process



- hydrogels swollen over night with 1 wt.% NaCl solution
- m(swollen polymer) = m(supernatant phase) = 0.5 m(total)
- degree of cross-linking, sulfonation and neutralization were varied
- occupied surface below c_0 = 1 wt.% NaCl represents salt reduction in mg

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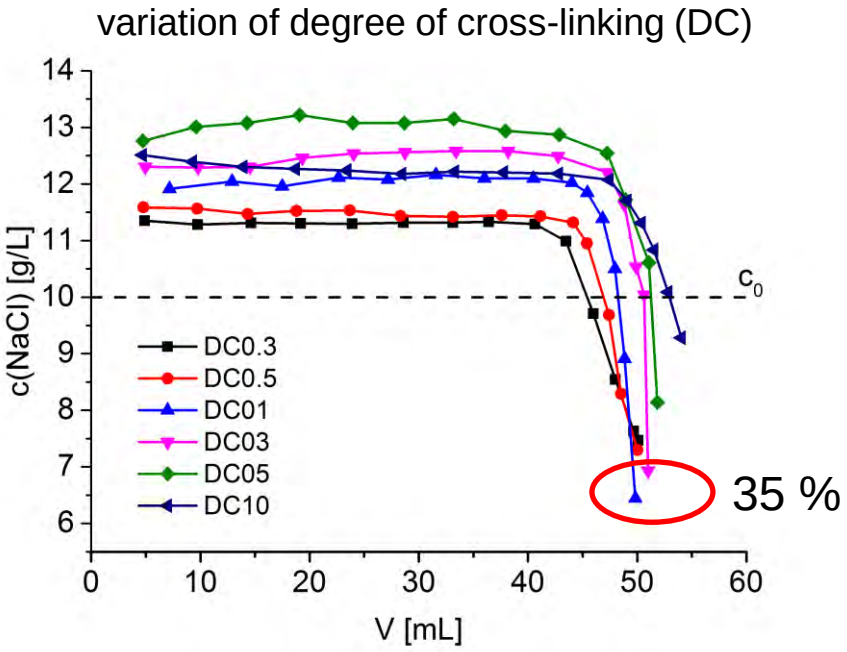
Desalination



- desalination up to 35 %
- higher degree of cross-linking

  higher salt repulsion

  worse total salt reduction

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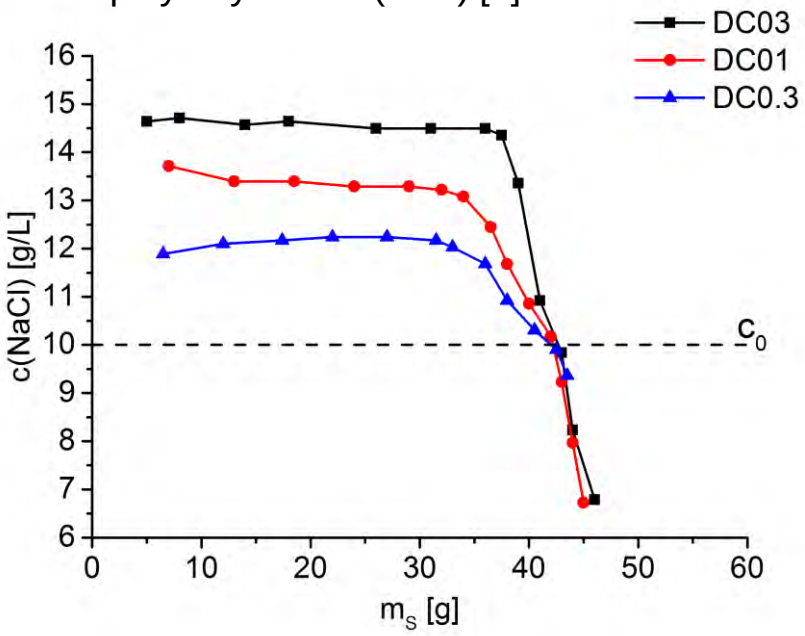
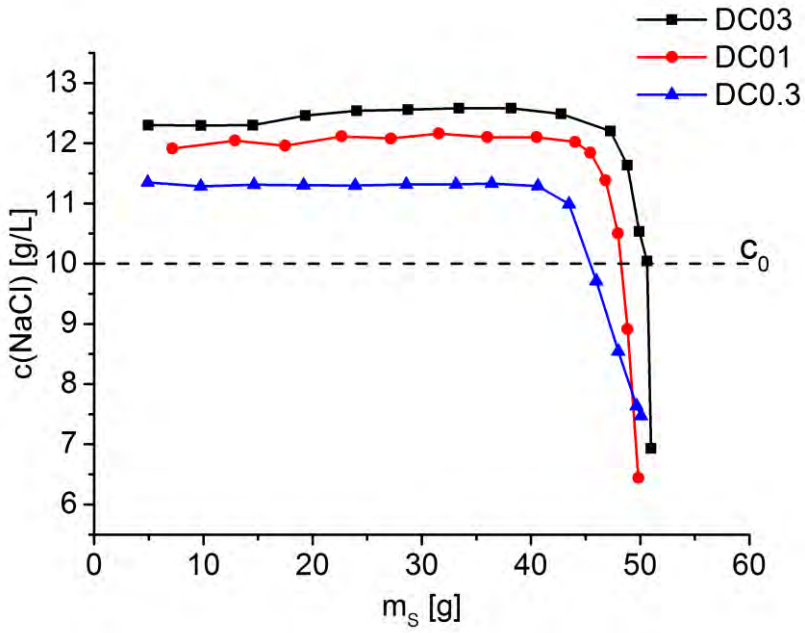
Desalination

polyacrylic acid (PAA) [6]



polystyrene sulfonate (PSS)



- better salt repulsion of PAA
- comparable desalination of DC1 PAA and DC0.3 PSS
- best results of PAA with high DC, best results of PSS with low DC

[6] Höpfner, Johannes (2009), Auswirkung von mechanischen Feldern und Drücken auf gequollene Polyacrylatnetzwerke, KIT. (diploma thesis)

Conclusions

- sulfonated polystyrene networks synthesized and characterized
- degree of cross-linking was varied
- desalination of 1 wt.% NaCl up to 35 %
- lower salt repulsion and degree of swelling than polyacrylic acid
- comparable degree of desalination

Control of Pore Size Distribution in Hydrogels

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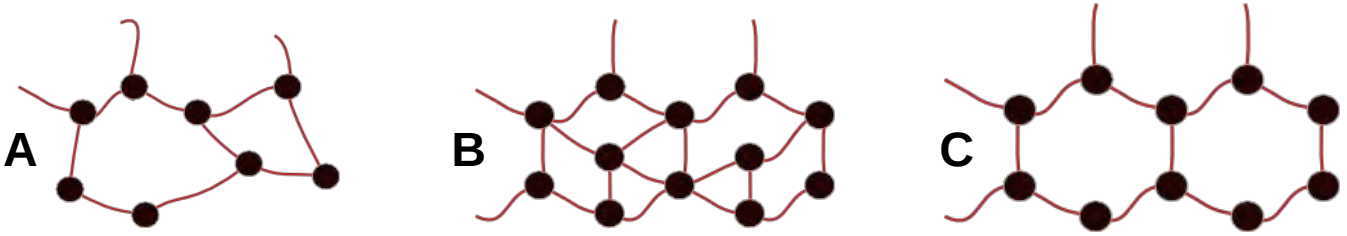
Ą System:



property	randomly cross-linked	quasi-model [7]	model - SFB 1176
elastic chains	broad size distribution	defined length	**defined length**
cross-link functionality	(fixed)	not fixed	**fixed**
pore size distribtuion	broad	middle	**small**

better defined system

more homogenous mesh size distribution

SFB 1176
Projekt C1

[7] A. Triftaridou et al., *Polymer Bulletin* **2007**, *58*, 185 -190.

Thank you for your attention