Modeling Volume Phase Transitions in Thermosensitive Hydrogels

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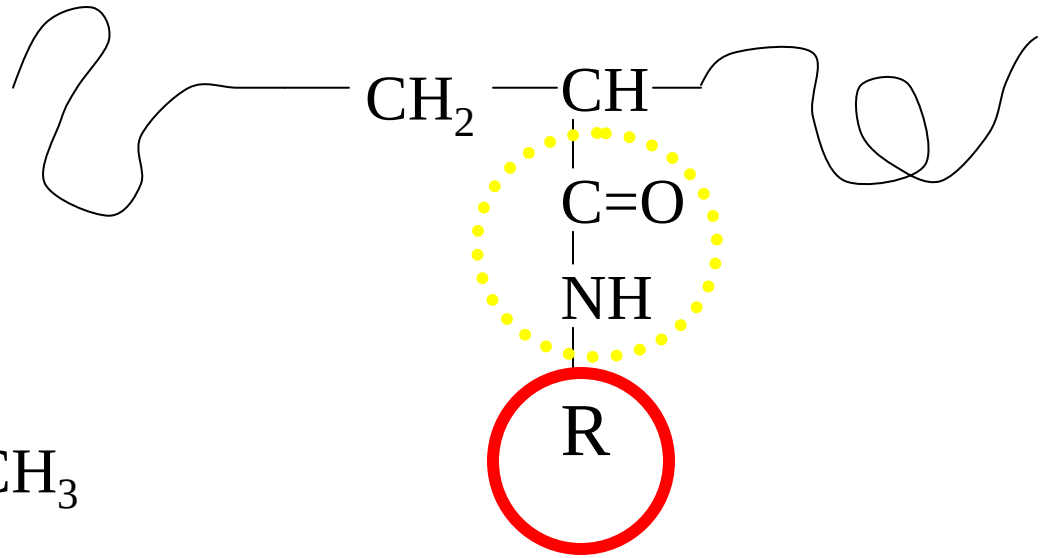
Relevance

- Intelligent gels
- Detergents
- “Zipping” in DNA & Bilayers in lipids
- Gel spinning (e.g. spider webs)
- Snail motions on lake surfaces
- Dissolution & phase separation

and many more…..

Theme

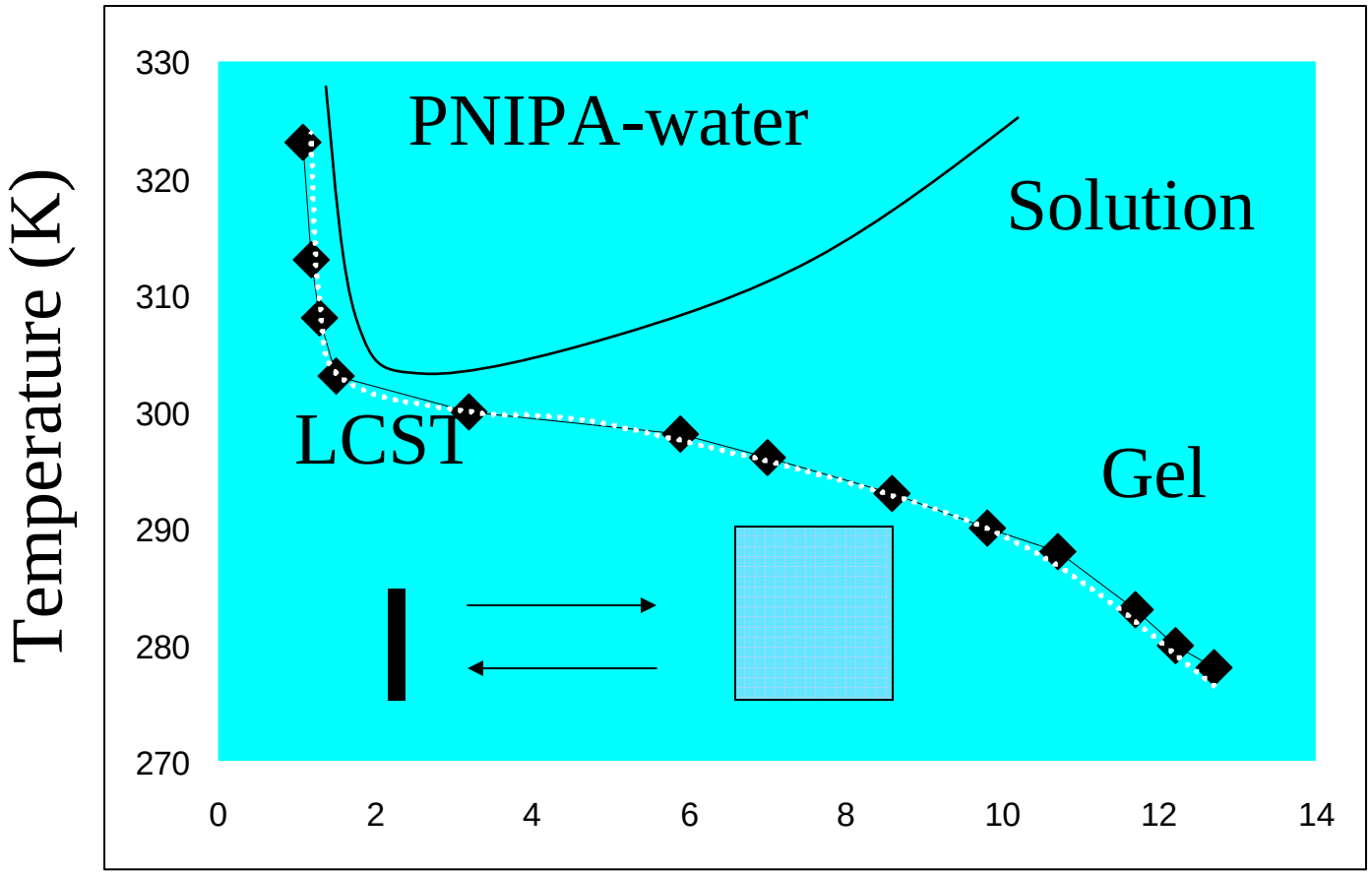
- **LCST-type Volume Transitions in Gels**
- **Deformation induced phase separation**



e.g.

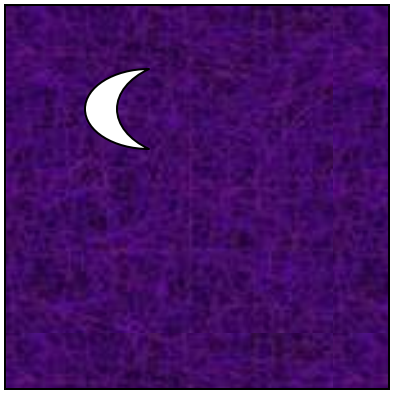
R = CH(CH_3)(CH_3)

PART-I
LCST-type volume transition

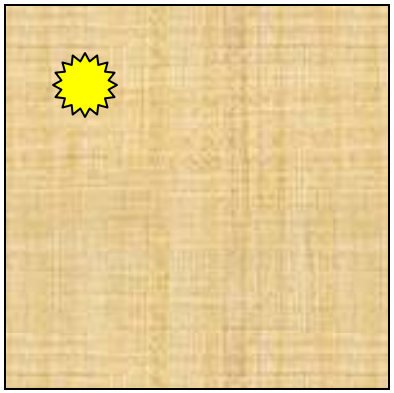


Novel Applications

Smart windows by “Cloud Gel” (Suntek Inc.)



light

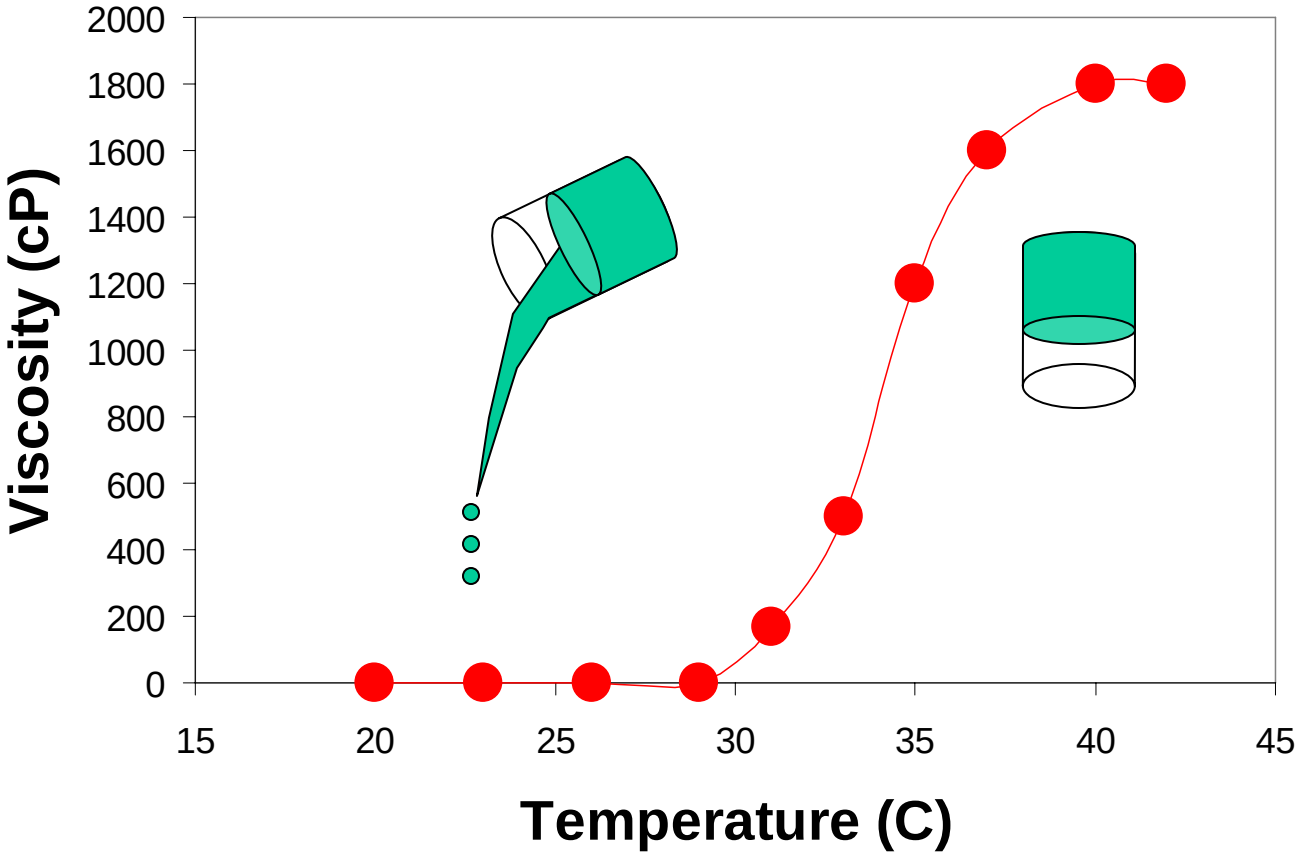


Transparent
at lower temp

Hazy
at higher temp

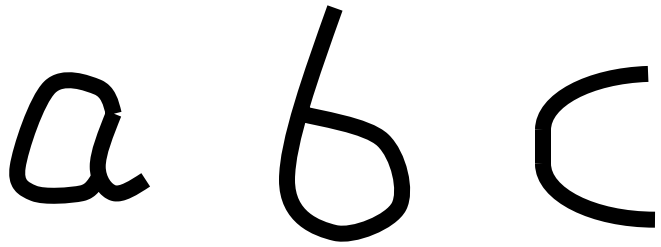
Novel Applications:

smart rheology for clutches

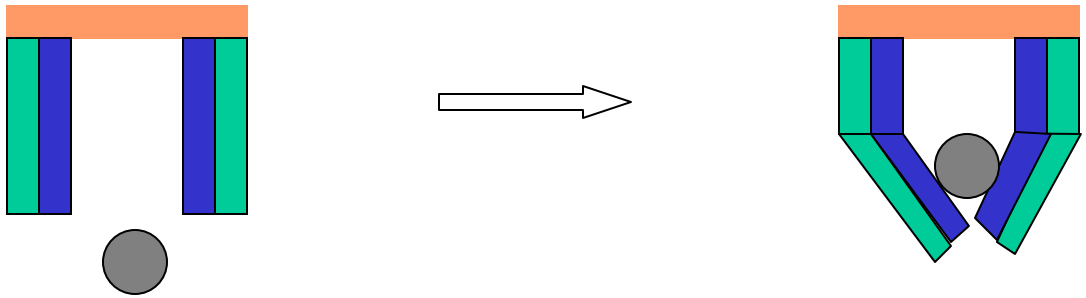


Novel Applications (Robotics)

- Bigel strips - bending gels **(Science, 269, 525 (1995))**



- Gel hand



Novel Applications (Control Drug delivery)

PMAA-g-PEG hydrogel + insulin + glucose oxidase

glucose

Gel + insulin + gluconic acid

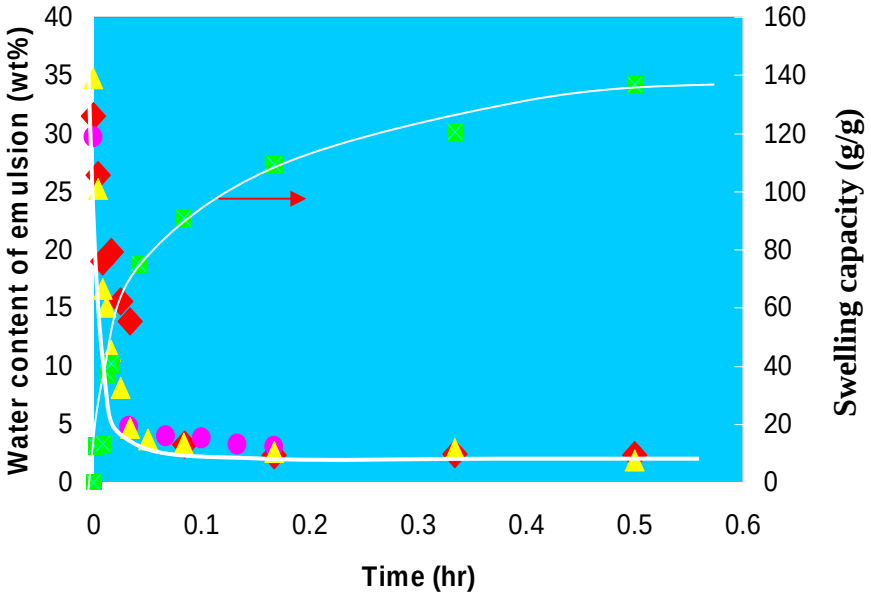
Swelling of gel

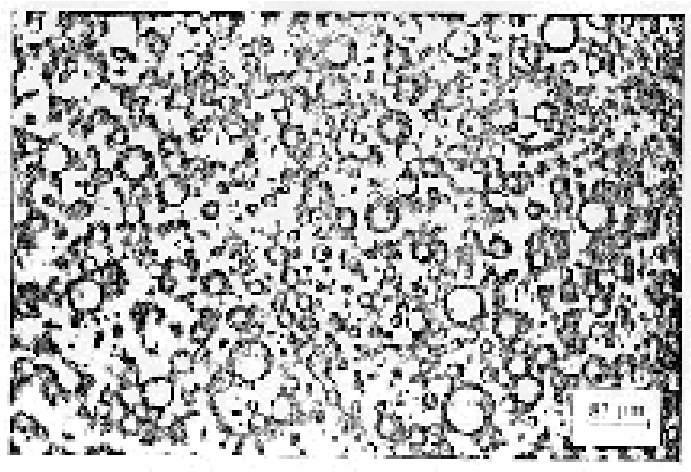
Release of insulin

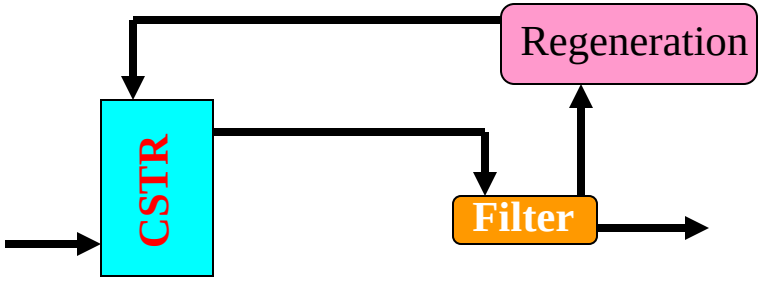
{ Dorski Hassan, Peppas et al. (Purdue Univ.) }

Novel Applications (Chemical separations)

OTD-Water separation (Buwa et al., IEC, 35, 4182 (1996))







The LCST-type volume transition occurs due to

- differences in compressibilities
- specific interactions (H-bonding, etc)

Flory theory of swollen networks

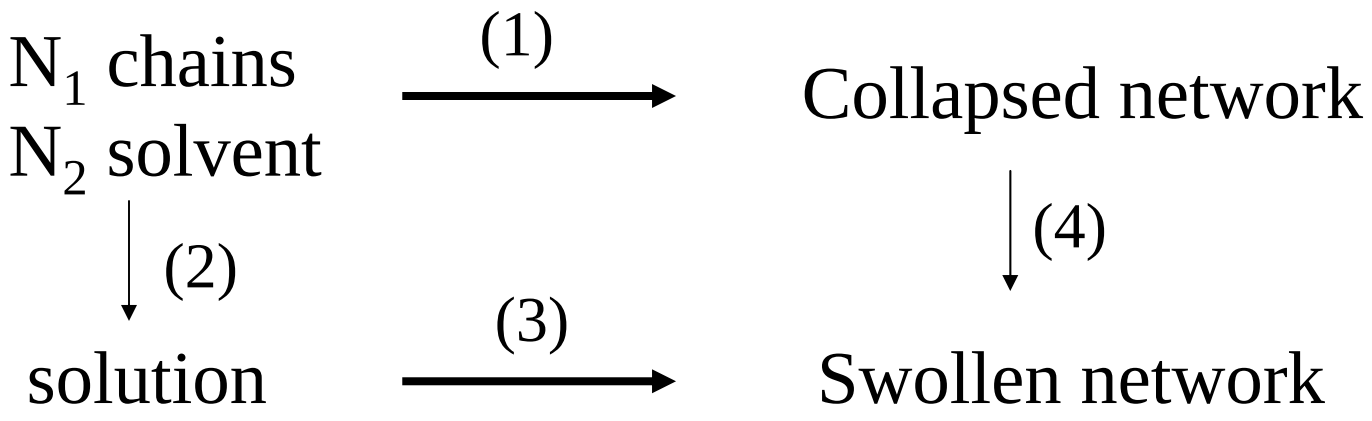
$$\pi = \mu_1 - \mu_1^o = 1 + \ln\phi_1 + \chi\phi_1\phi_2 + \left(\frac{\nu_e}{V_o}\right)\vartheta\left[\left(\frac{V_o}{V}\right)^{1/3} - \frac{1}{2}\left(\frac{V_o}{V}\right)\right] = 0$$

is not applicable !

Objective

- To understand the fundamental causes for the LCST-volume transitions
- The role of H-bonding & Hydrophobic interactions
- To be able to synthesize “tailored” smart gels

The Extended Lattice-Fluid-Hydrogen-Bond (LFHB) model



$$\Delta G^{(4)} = \Delta G^{(2)}_{LFHB} + \Delta G^{(3)-(1)}_{El}$$

- LFHB : Panayiotou & Sanchez, JPC, 95, 10090 (1991)
- Elastic : Flory-Rehner, Principles of Polym. Chem.

LFHB theory

- decoupling of H-bonding and ‘other’ interactions
- mean-field interaction energy

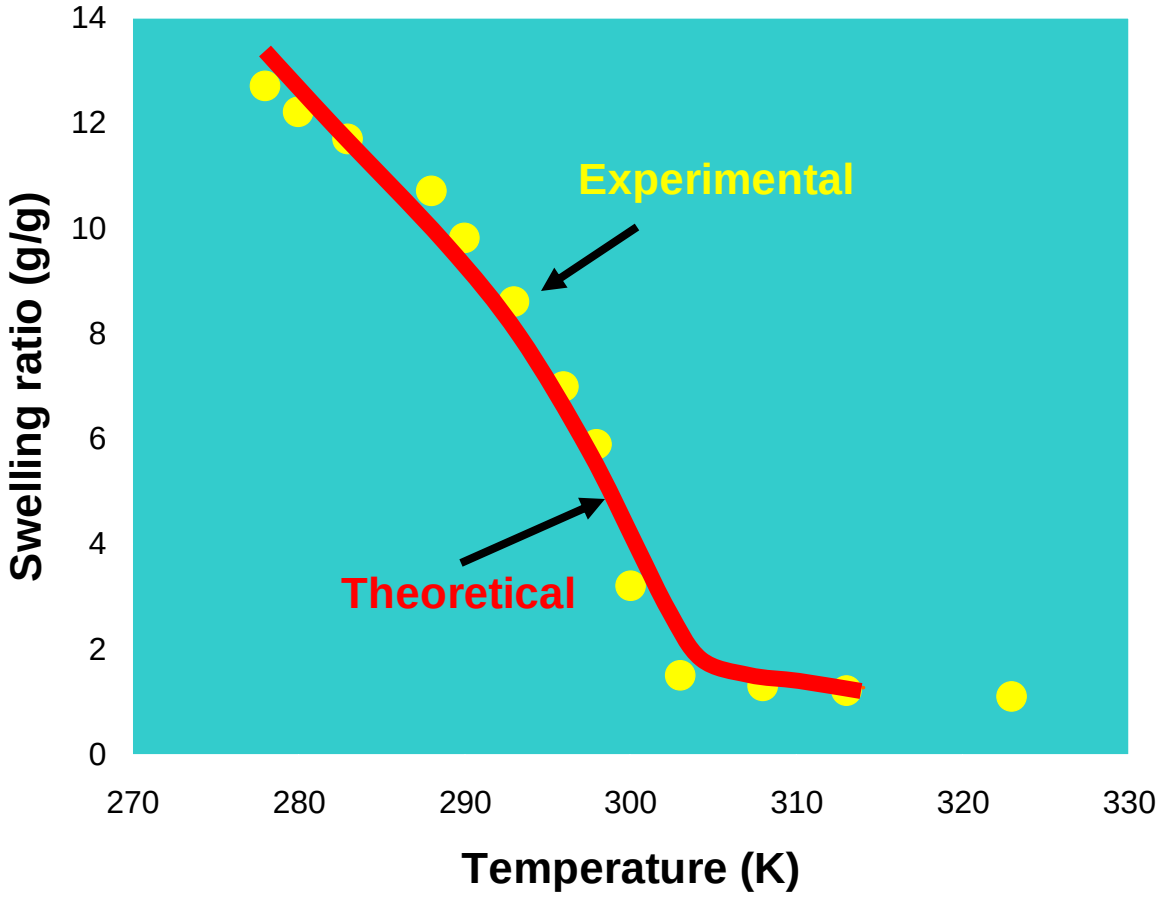
$$\frac{\mu_1}{RT} = \ln\left(\phi_1 / \omega_1\right) + \left(1 - \frac{r_1}{r_2}\right)\phi_2 + r_1\tilde{\rho}\phi_2^2 X_{12} + r_1\left\{-\frac{\tilde{\rho}}{\tilde{T}_1} + \frac{\tilde{P}_1\tilde{v}}{\tilde{T}_1} + \left(\tilde{v} - 1\right)\ln(1-\tilde{\rho}) + \frac{1}{r_1}\ln\tilde{\rho}\right\}$$

$$+ r_1\sum_i^m\sum_j^n \nu_{ij} - \sum d_i^1 \ln\frac{\nu_d^i}{\nu_{io}} - \sum a_j^1 \ln\frac{\nu_a^j}{\nu_{oj}} - \sum a_j^1 \ln\frac{\nu_a^j}{\nu_{oj}} + \left\{r_1\left(\frac{\nu_e}{V_o}\right)v_1^*\tilde{v}\left[\left(\frac{V_o}{V}\right)^{1/3} - \frac{1}{2}\left(\frac{V_o}{V}\right)\right]\right\}$$

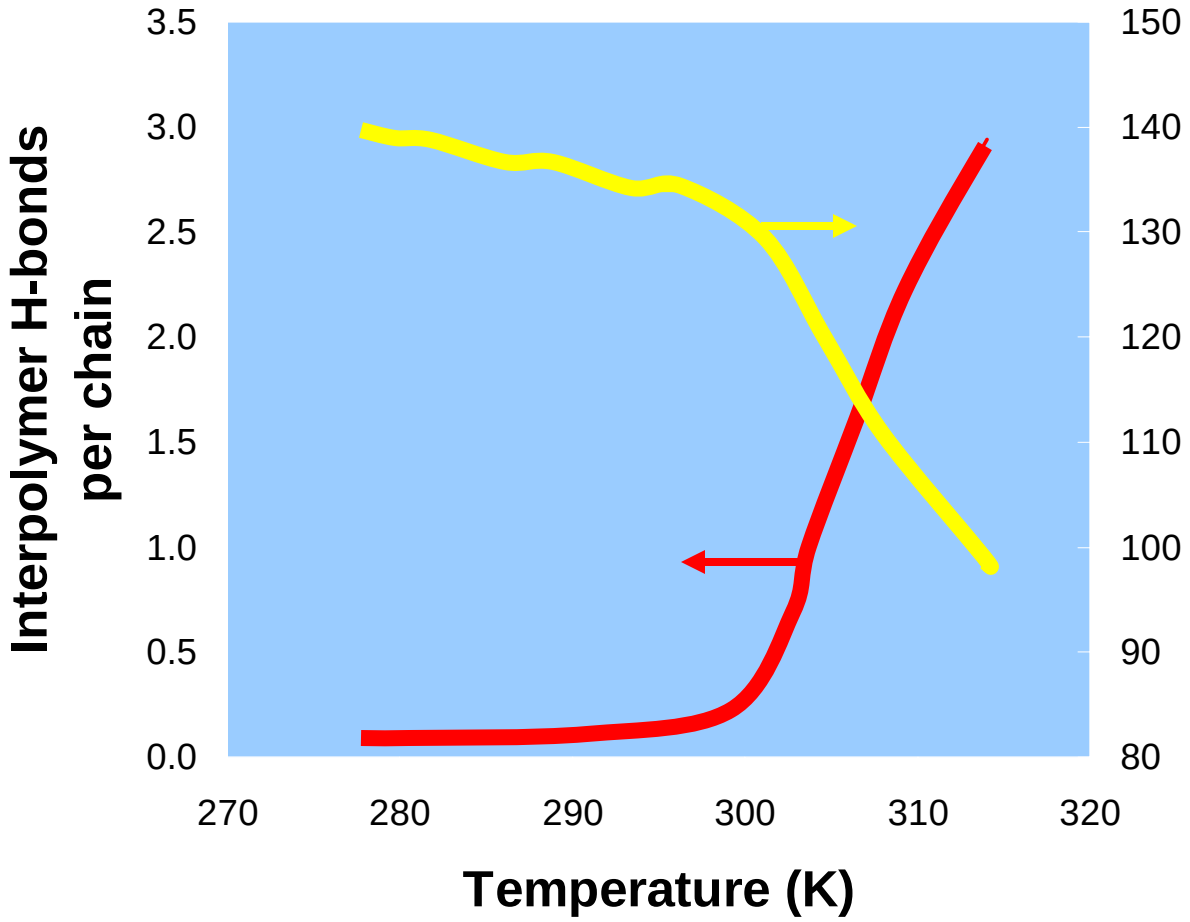
$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left\{\ln\left(1-\tilde{\rho}\right) + \tilde{\rho}\left[1 - \left(\frac{1}{r} - \sum_i^m\sum_j^n \nu_{ij}\right)\right]\right\} + \frac{\nu_e}{V_o}\tilde{T}v^*\left[\left(\frac{V_o}{V}\right)^{1/3} - \frac{1}{2}\left(\frac{V_o}{V}\right)\right] = 0$$

$$\nu_{ij} = \nu_{io}\nu_{oj}\tilde{\rho}\,\exp\left(-G_{ij}^o / RT\right)$$

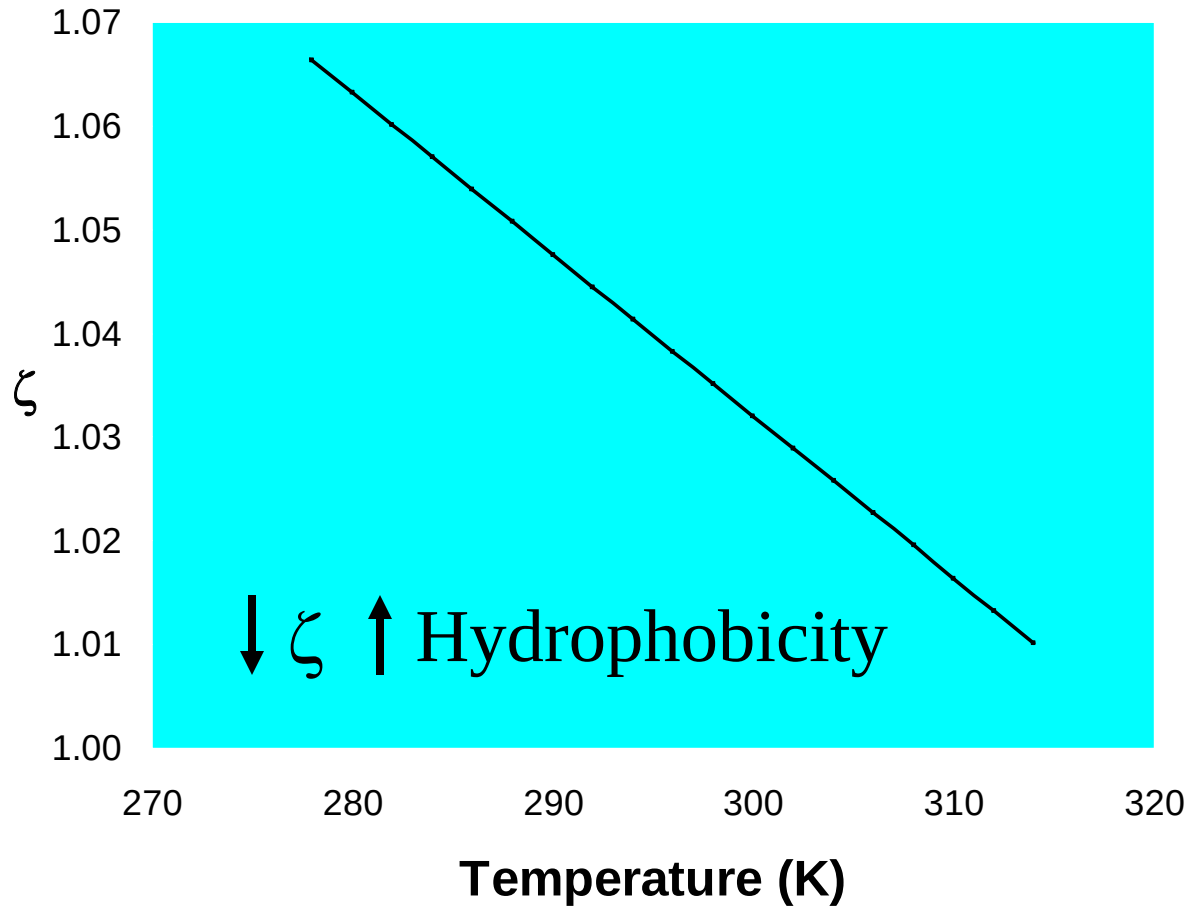
PNIPAm Gel :Volume Transition



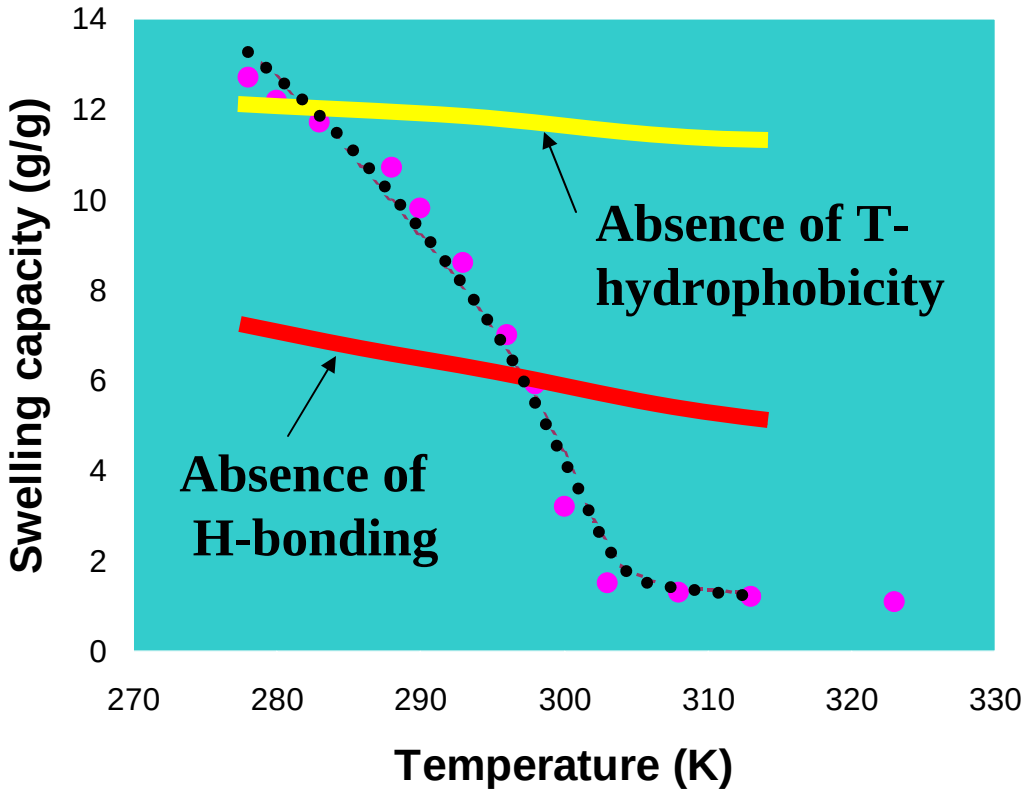
PNIPAm Gel : H-bonding rearrangement



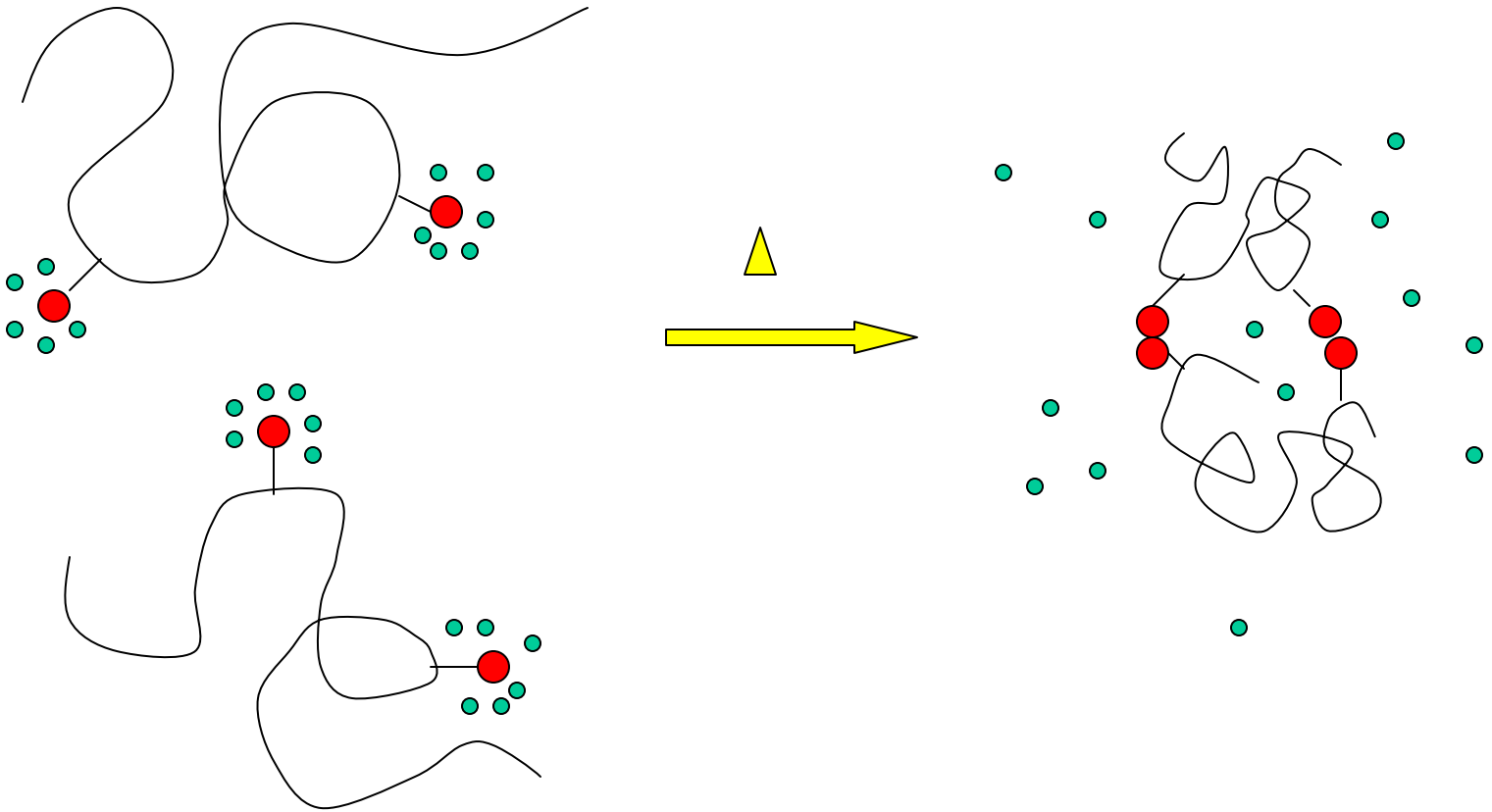
PNIPAm Gel : Hydrophobicity



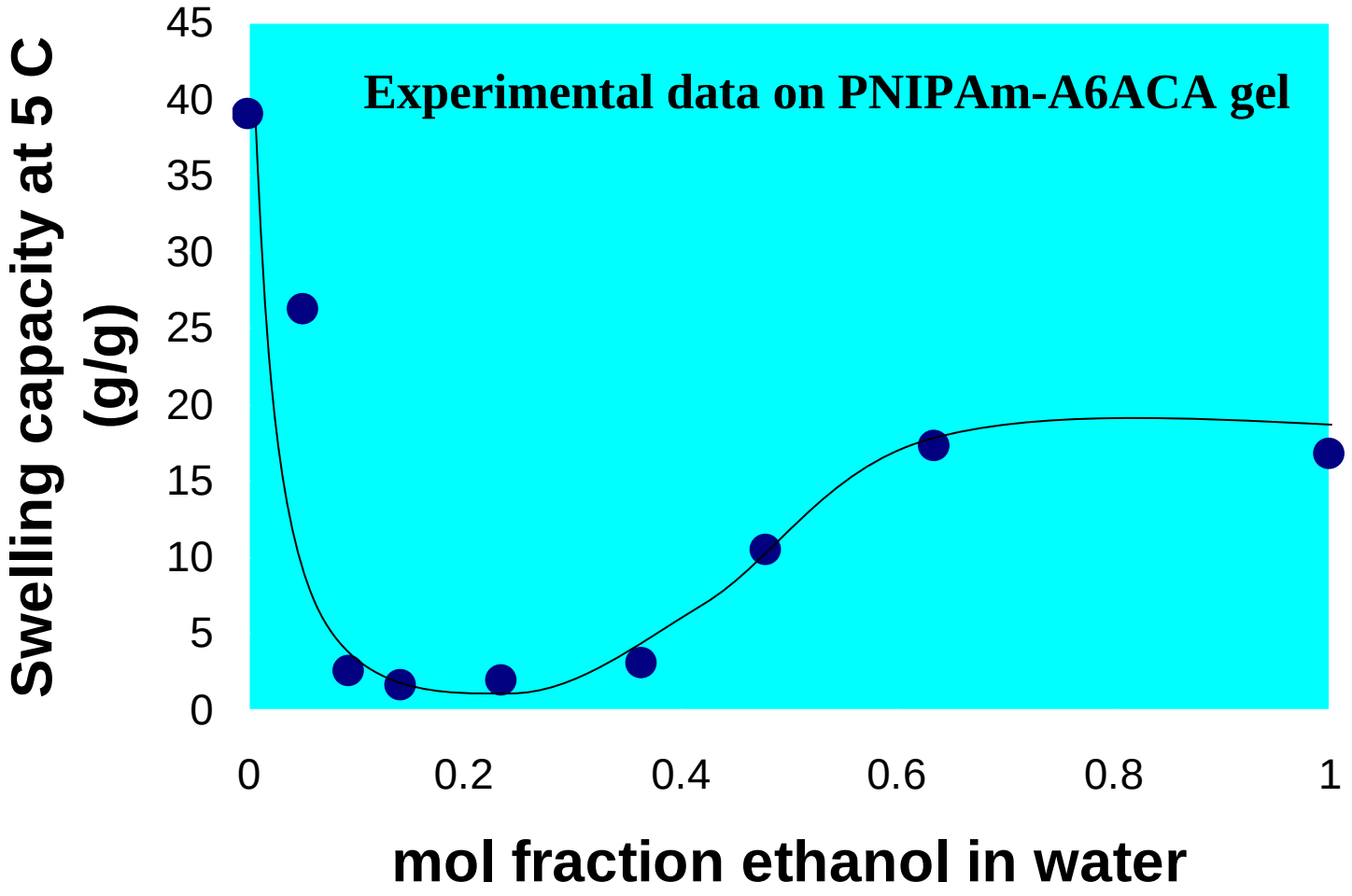
PNIPAm gel : role of H-bonding and Hydrophobicity



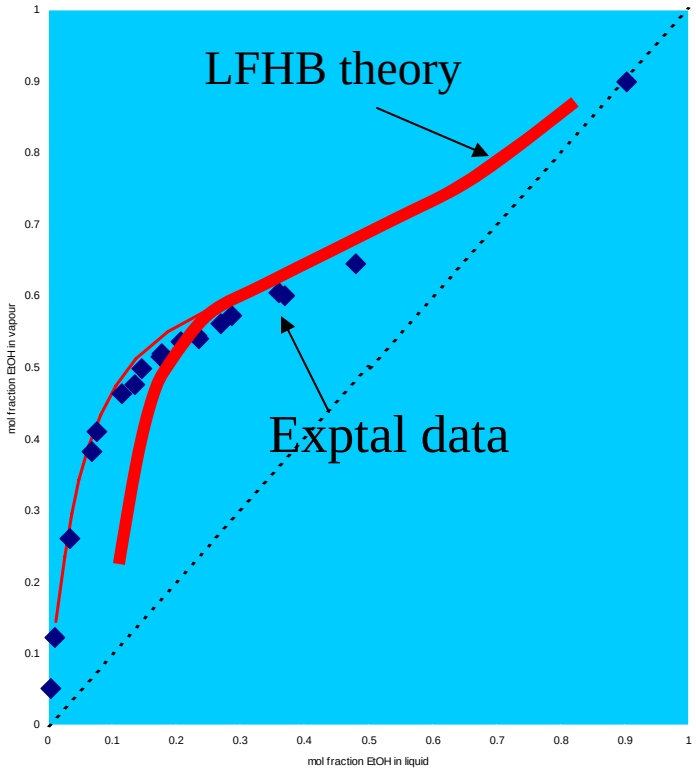
Mechanism of volume transition

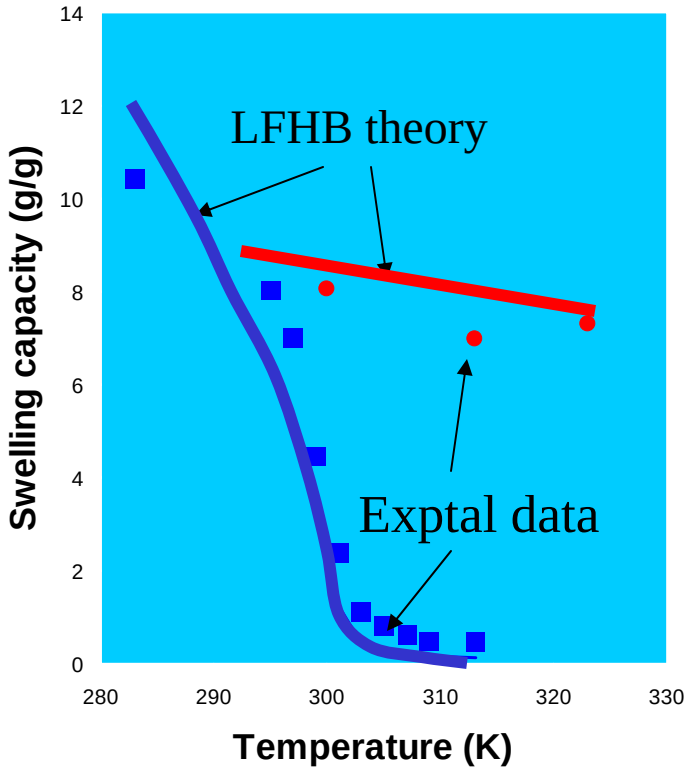


Re-entrant volume transition of PNIPAm in Ethanol-Water {Lele et al., JCP, 107, 2142 (1997)}



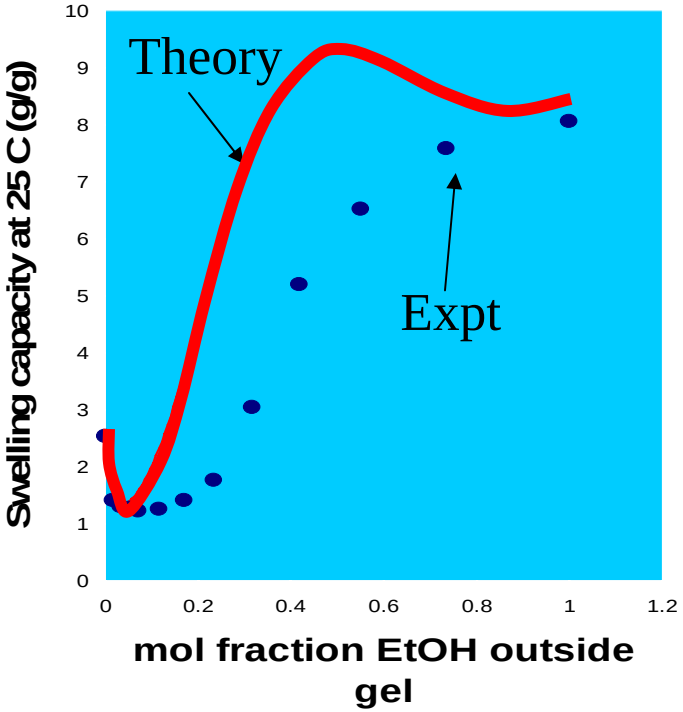
Re-entrant volume transition : determination of model parameters

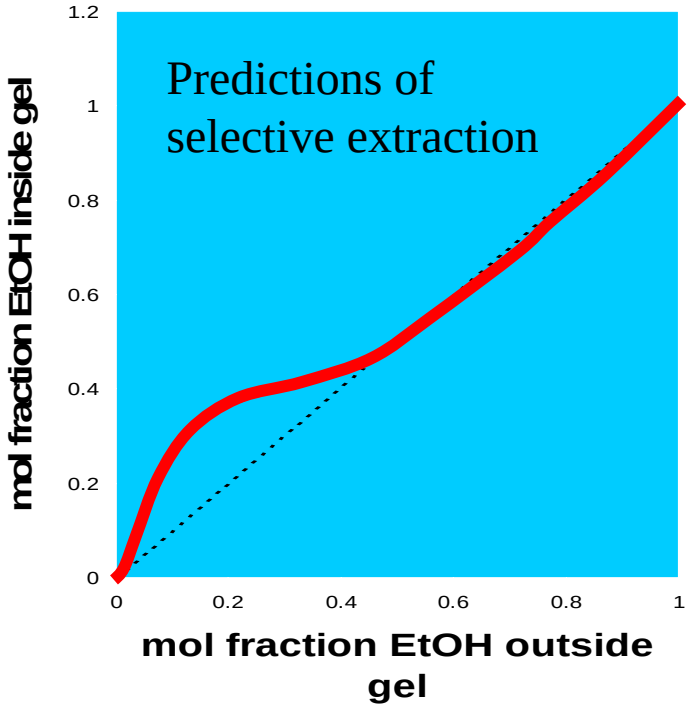




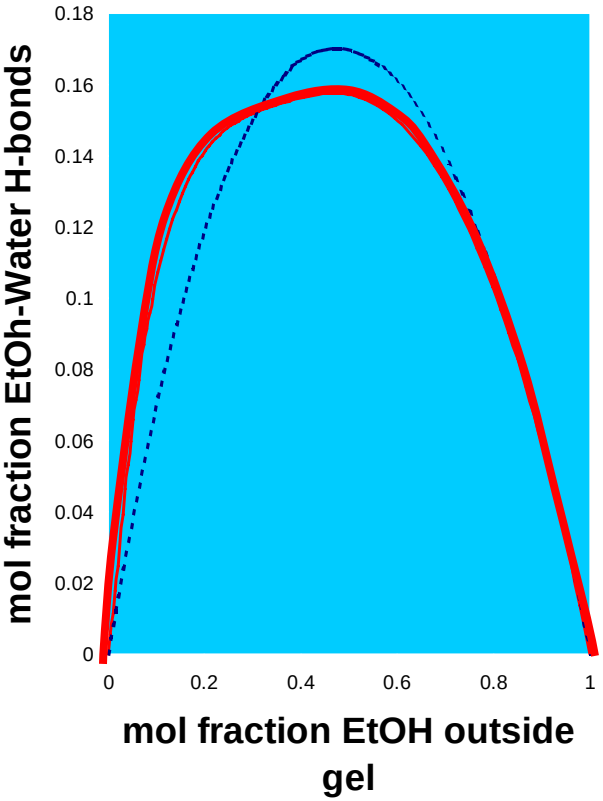
Re-entrant volume transition : predictions of extended LFHB model

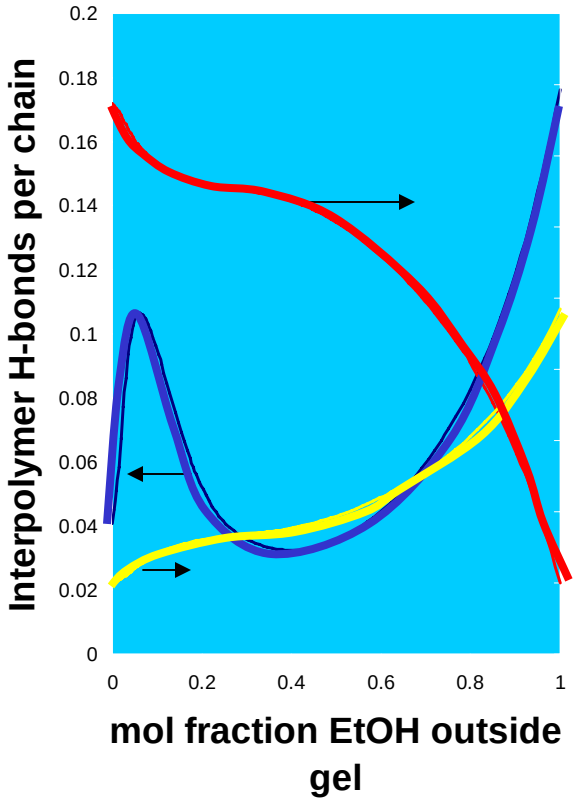
$$\left(\mu_w\right)^{Gel} = \left(\mu_w\right)^{Out}$$
$$\left(\mu_e\right)^{Gel} = \left(\mu_e\right)^{Out}$$





Re-entrant volume transition : molecular causes



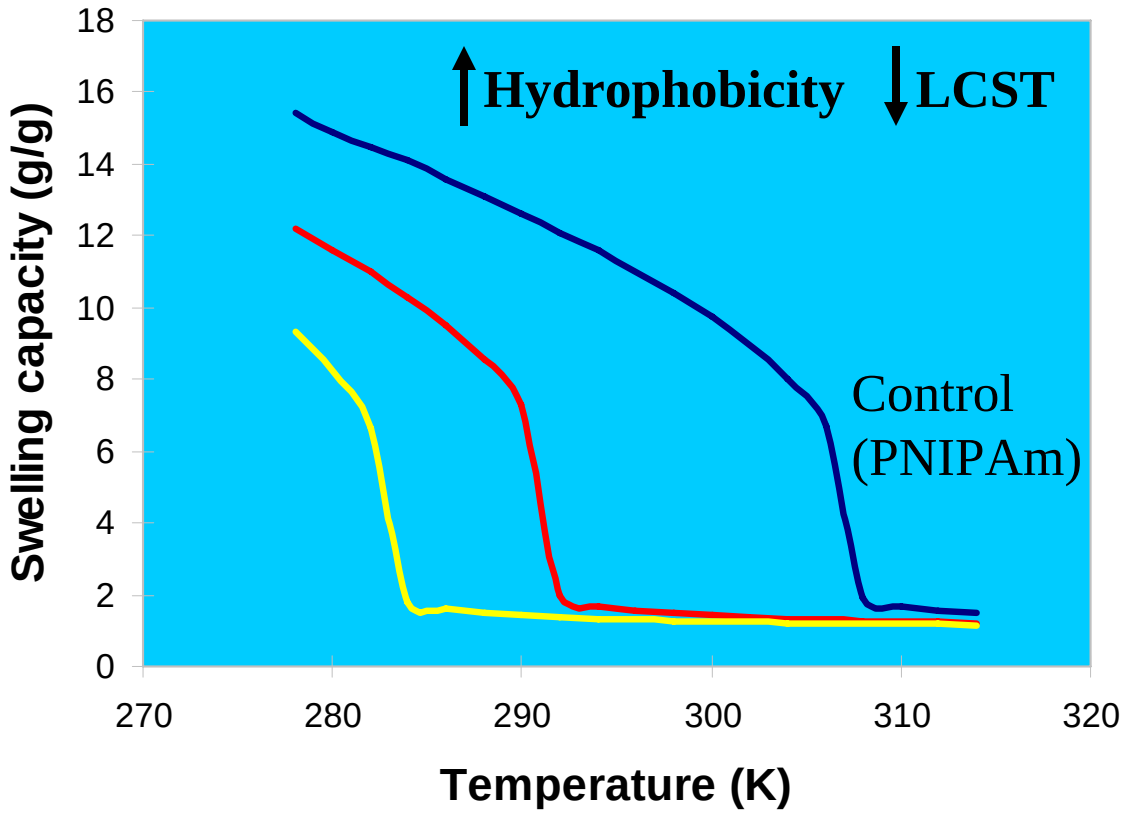


So far so good !!

But so what ???

Tailoring of gels : Hydrophobicity

{ Lele et al., JCP, 106, 2142 (1997) }



Tailoring of gels : Hydrophilicity

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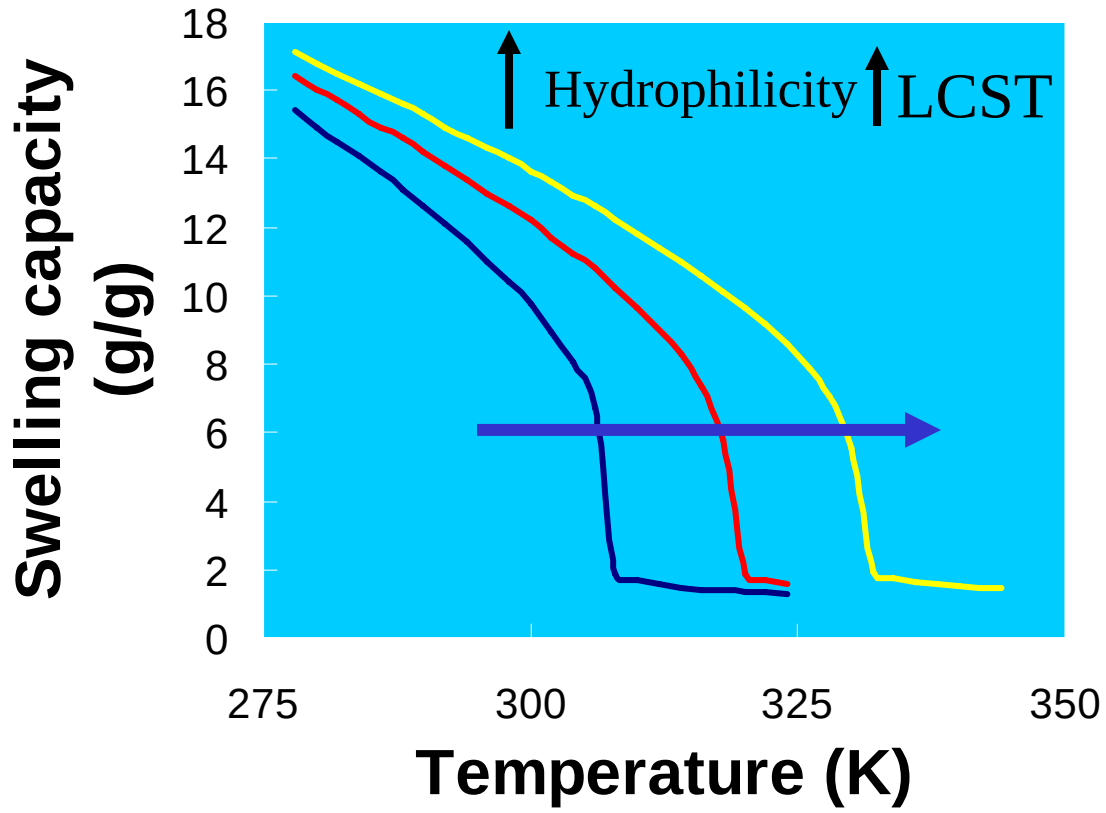
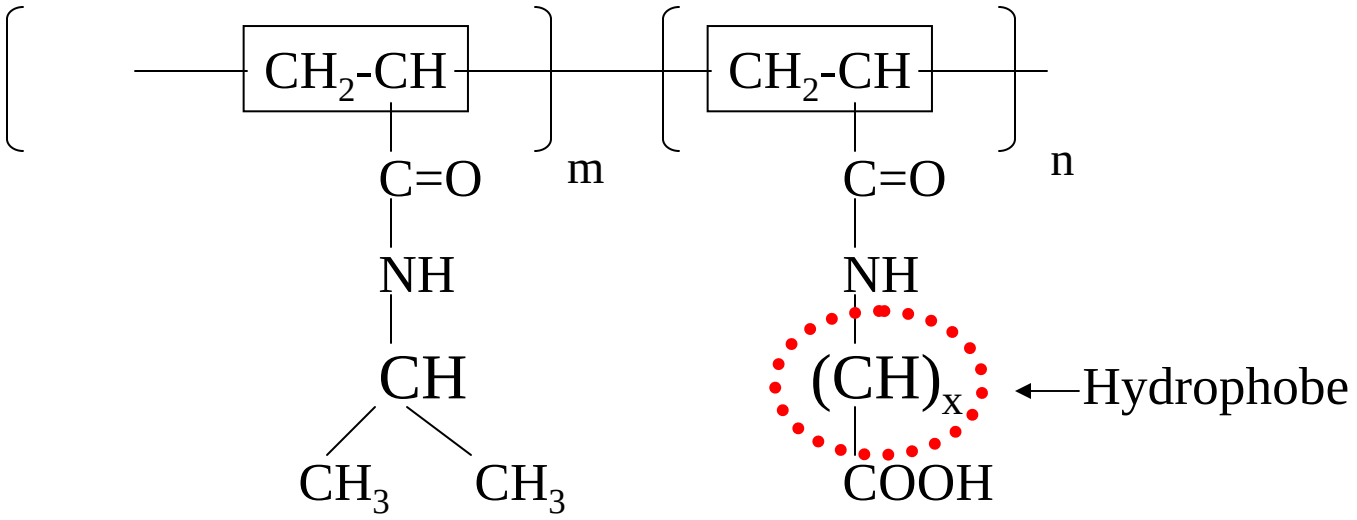


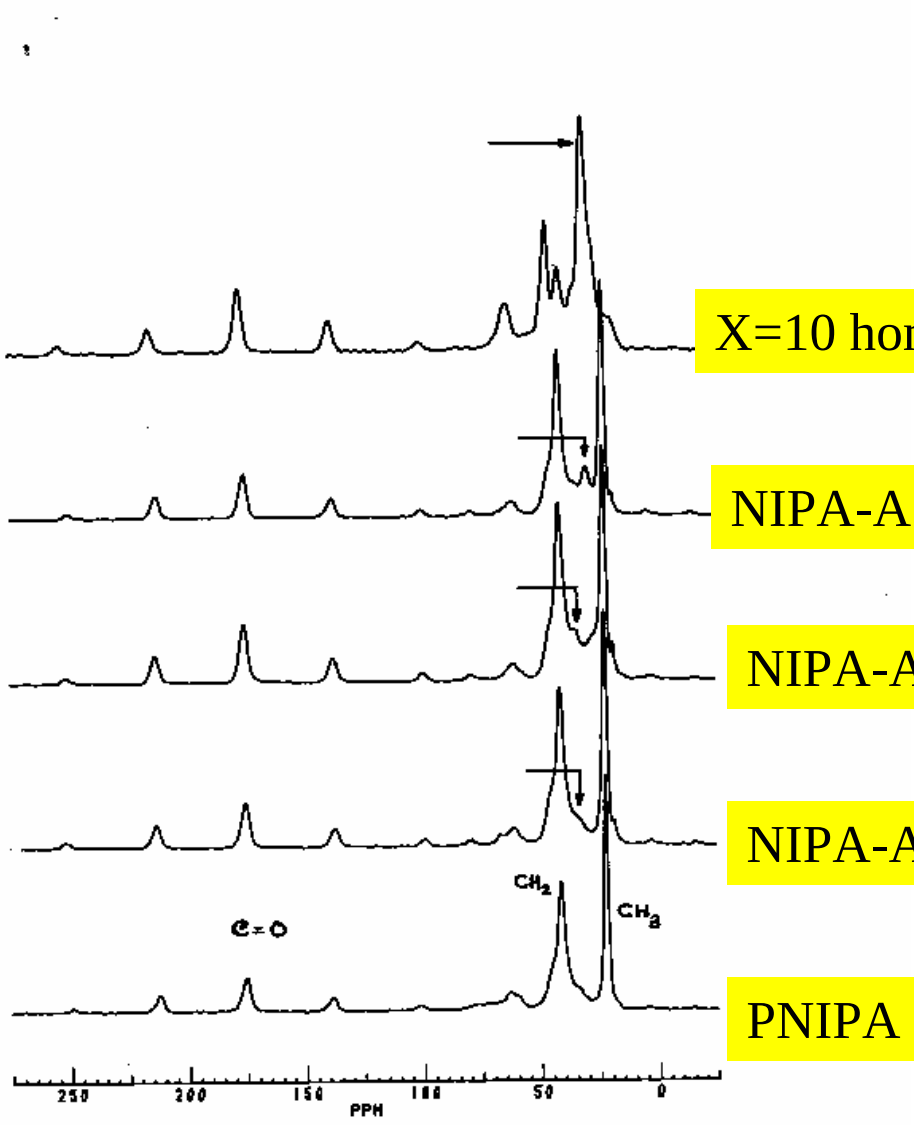
Tailoring of gels : Effect of comonomers

{ Badiger et al., to be submitted to Macromolecules }

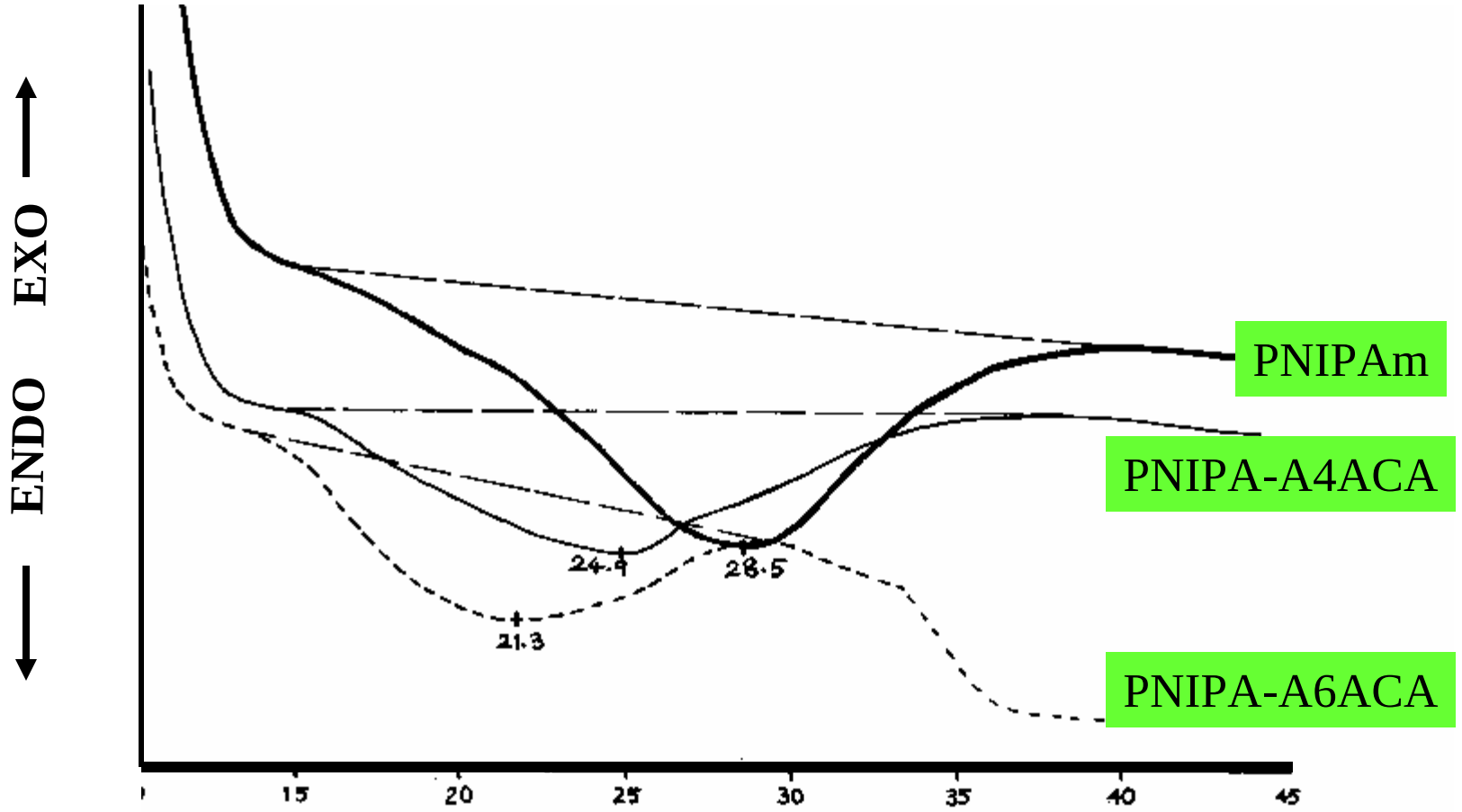


x=3 : A4ACA
x=5 : A6ACA
x=10 : A11ACA

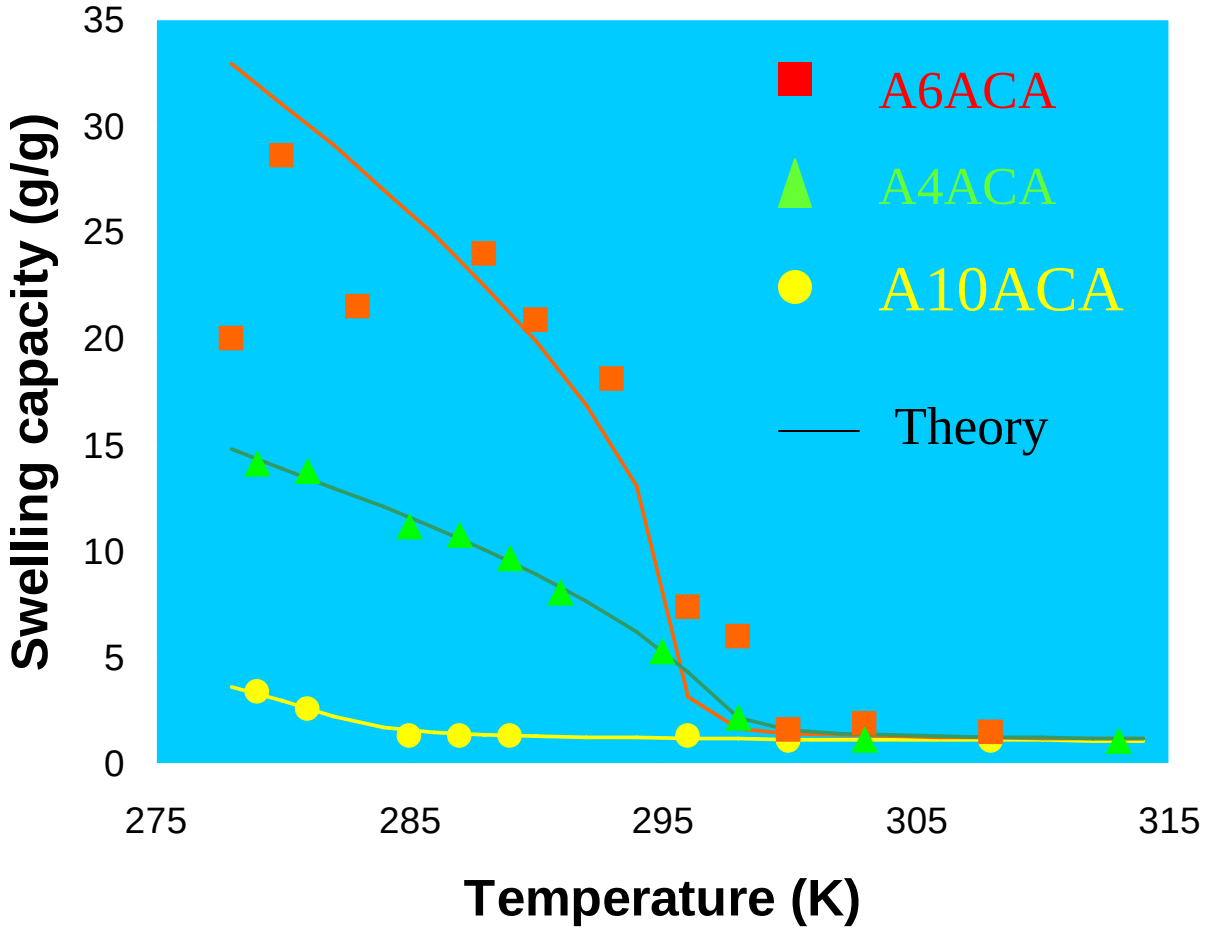
^{13}C CP-MASS spectra of copolymer gels (MSL-300 FT-NMR)



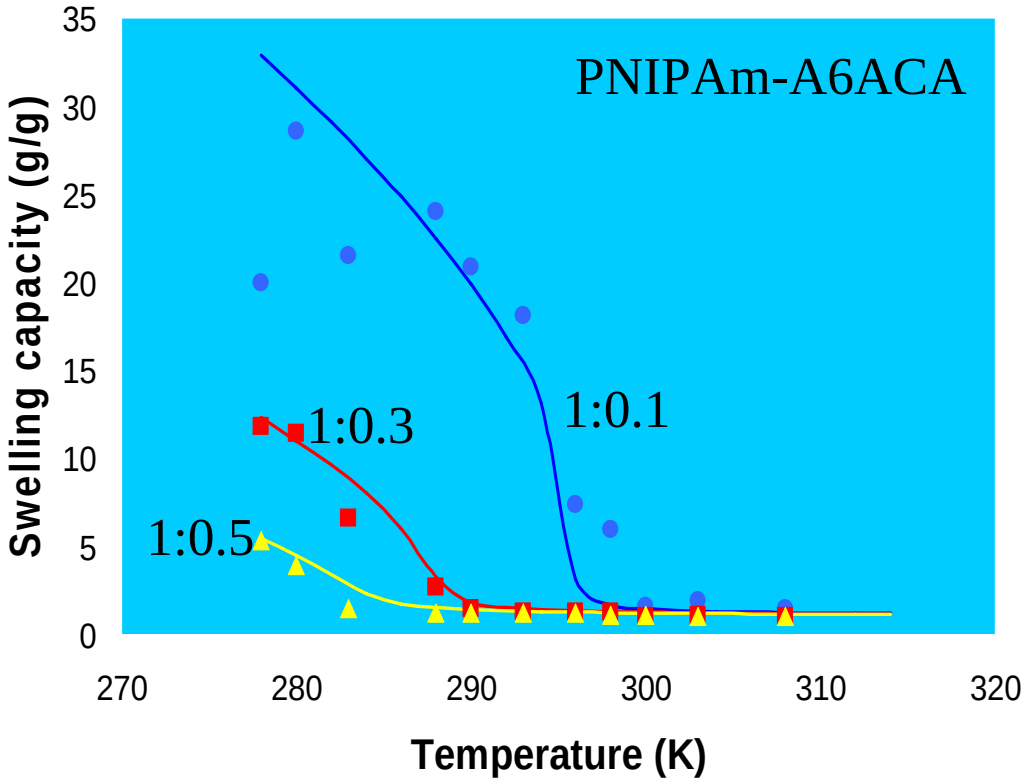
DSC


ENDO
EXO
24.9
28.5
21.3
15
20
25
30
35
40
45
PNIPAm
PNIPA-A4ACA
PNIPA-A6ACA

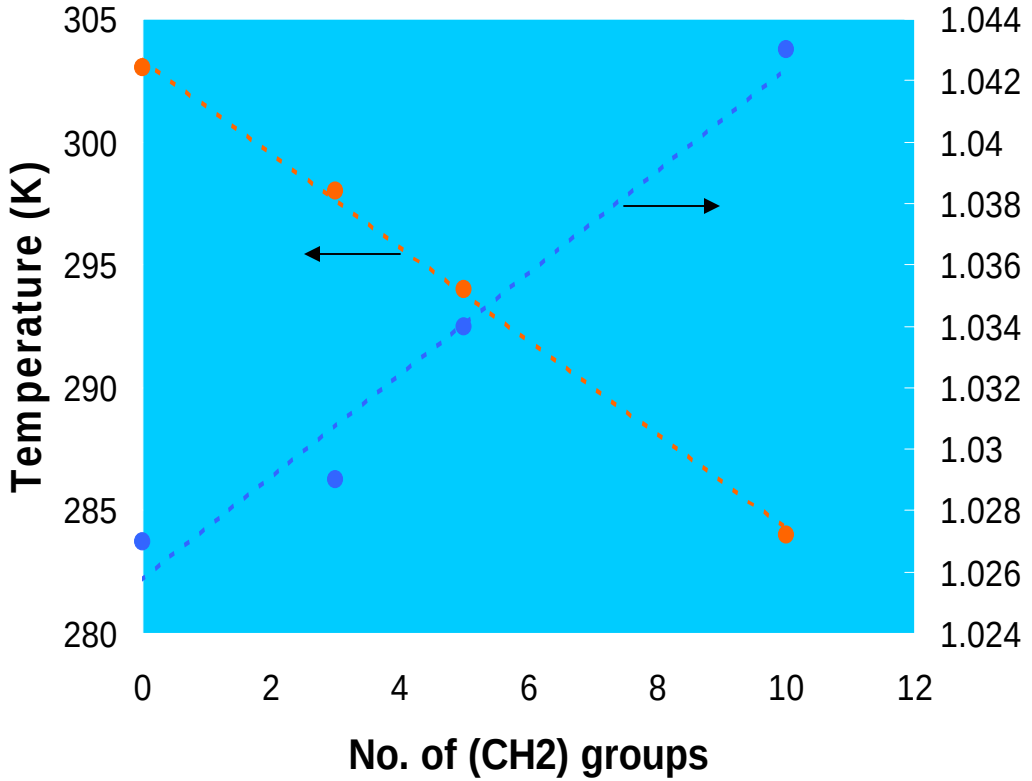
Tailoring of gels : Effect of comonomers



Tailoring of gels : Effect of comonomers



Tailoring of gels : correlations



In Summary:

- **Critical Hydrophobic - Hydrophilic balance**
- **Quantitative predictions of extended LFHB**
- **Macroscopic Volume transition** → **Microscopic causes**
- **Possibility of "Tailoring" of gels**

Publications

- Varghese, S.; Lele, A. K.; Srinivas, D.; Sastry, M.; Mashelkar, R. A. Novel macroscopic self-organization in polymer gels, *Adv. Matl*. 2001, *13*, 1544-1548.
- Varghese, S.; Lele, A. K.; Srinivas, D.; Mashelkar, R. A. Role of hydrophobicity on structure of polymer-metal complexes, *Journal of Physical Chemistry B* 2001, *105*, 5368-5373.
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- Bhalerao, V. S.; Varghese, S. V.; Lele, A. K.; Badiger, M. V. Thermoreversible hydrogel based on radiation induced copolymerization of poly(N-isopropyl acrylamide) and poly(ehtylene oxide), *Polymer* **1998**, *39*, 2255-2260.
- Lele, A. K.; Karode, S.; Badiger, M. V.; Mashelkar, R. A. Predictions of re-entrant swelling behavior of poly(N-isoporpyl acrylamide) gel in a mixture of ethanol-water using lattice-fluid-hydrogen-bond theory, *J. Chem. Phys.* **1997**, *107*, 2142-2148.
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- Varma, A. J.; Lele, A. K.; Mashelkar, R. A. Separations based on chemically selective polymer gels, *Chem. Eng. Sci.* **1995**, *50*, 3835-3838.
- Lele, A. K.; Badiger, M. V.; Hirve, M. M.; Mashelkar, R. A. Thermodynamics of hydrogen-bonded polymer gel-solvent systems, *Chem. Eng. Sci.* **1995**, *50*, 3535-3545.
- Badiger, M. V.; Lele, A. K.; Kulkarni, M. G.; Mashelkar, R. A. Swelling and phase transitions in deforming polymeric gels, *Ind. Eng. Chem. Res*. **1994**, *33*, 2426-2433.

Collaborators

- Dr R A Mashelkar
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