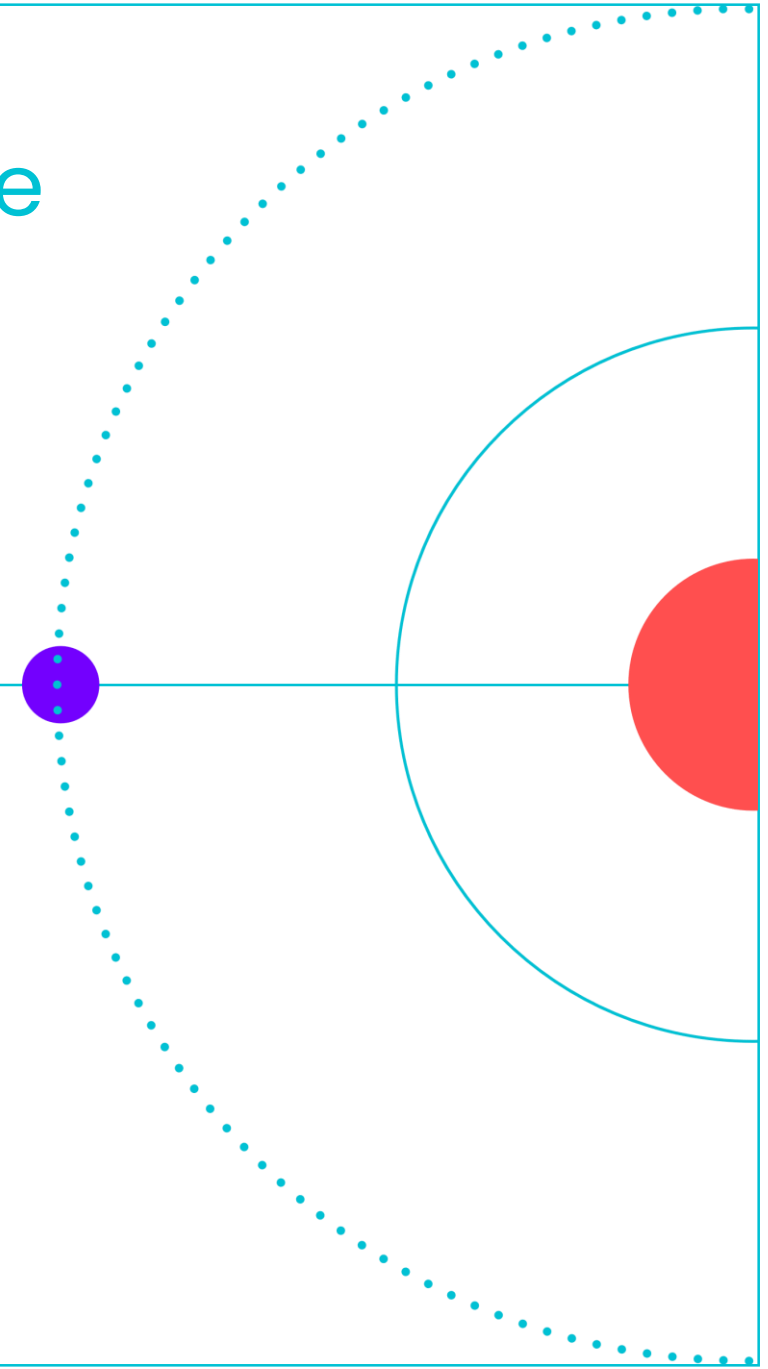
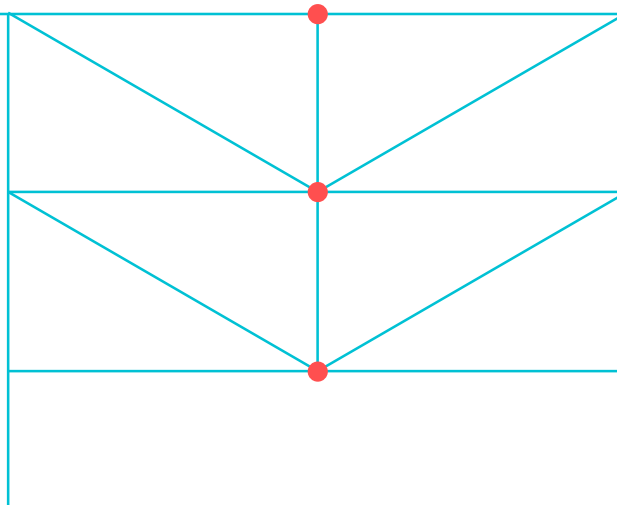


# Phase Equilibria in Stimuli-Responsive Gels: A PC-SAFT and Molecular Dynamics Study of Smart PNiPAAm Gels

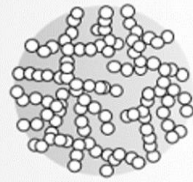
**TUHH**  
Technische  
Universität  
Hamburg



K. M. Eckert, X. Hu, I. Smirnova, W. G. Chapman

# Introduction: Gel Processing at TUHH

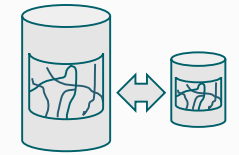
## Aerogels: Nanoporous, lightweight, super-insulation material



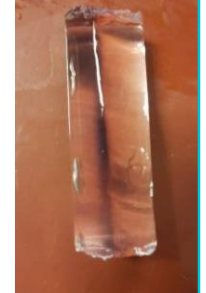
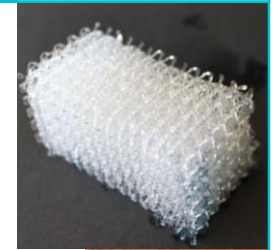
- Gel shape: Particles preferred
- Scale-up plans: 1500 lt./year for application in NZBs
- Production steps:
  1. Gelation
  2. Solvent exchange
  3. Supercritical drying: preserve pore structure



## Stimuli-Responsive Gels: Swelling and shrinkage on macroscopic level

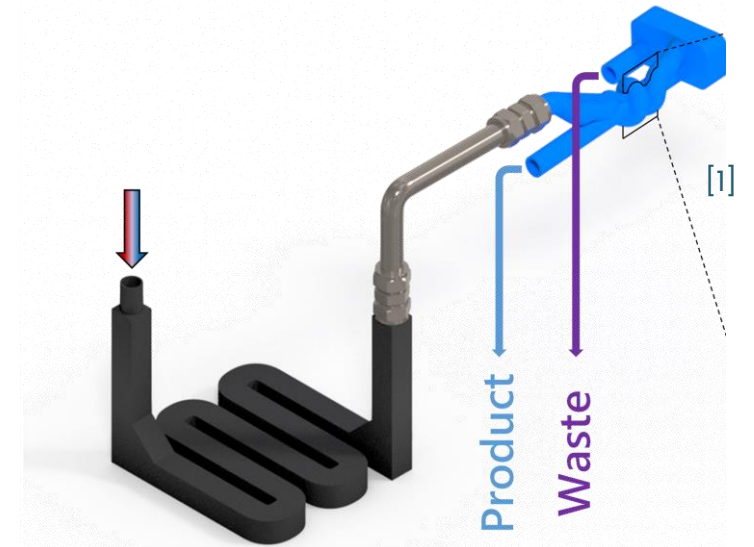
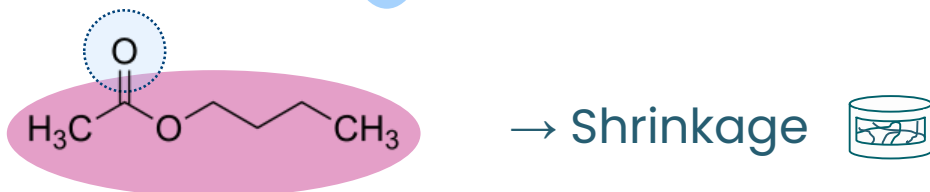


- Gel shape: Monoliths or 3D-printed structures
- Change in thermodynamic equilibrium as trigger
  - Expels and absorbs solvent through transition
- Responsibility enables self-regulating reaction system



# Introduction: Stimuli-responsive Gels

- Thermally induced actuation:  $f(T)$ 
  - Swelling & shrinkage regulate state
- Solvent interactions for actuation  $f(x_i)$ 
  - Interactions of functional groups



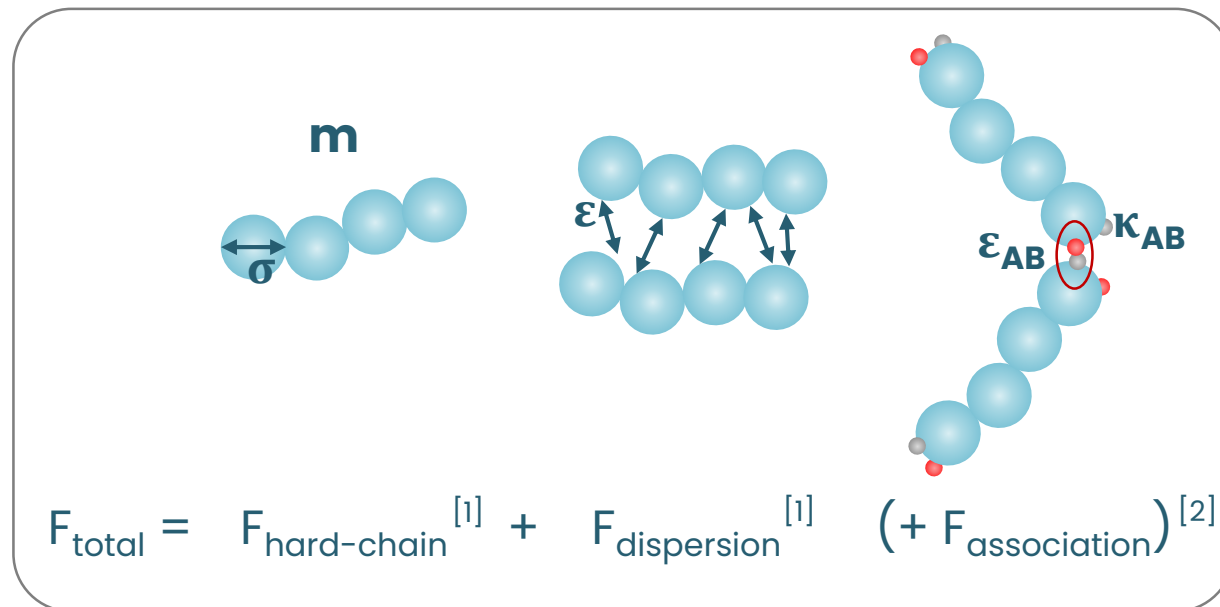
**Next Step:** Smart Reactor with  
reaction-triggered actuation

➤ Better understanding necessary

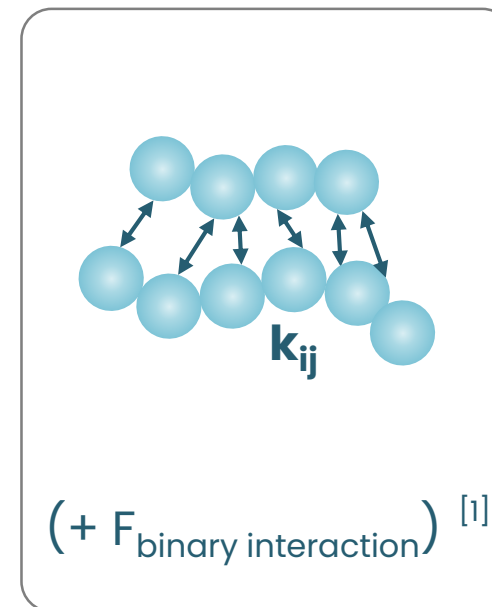
# Modeling Gel Systems with PC-SAFT

- Calculation of equilibria as liquid-liquid equilibria (LLE)
- Modification of PC-SAFT by applying additional Network model:

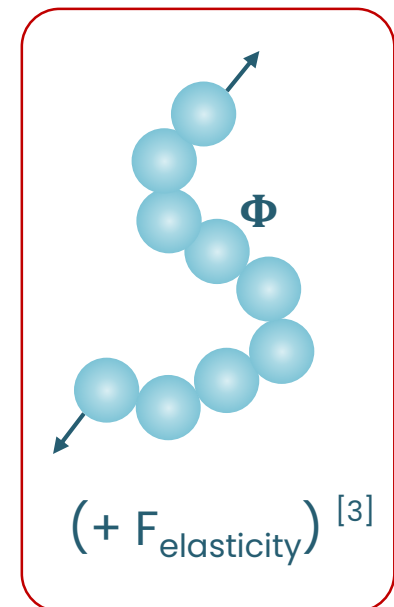
## Pure components



## Mixtures



## Network model



[1] J. Gross, G. Sadowski, Ind. Eng. Chem. Res. 2001

[2] J. Gross, G. Sadowski, Ind. Eng. Chem. Res. 2002

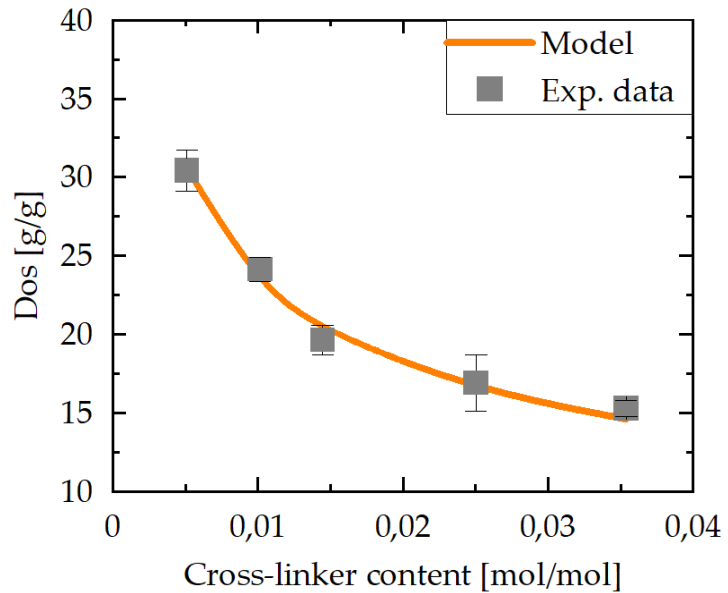
[3] M. C. Arndt, Dissertation, TU Dortmund

# Modeling Binary Systems with PC-SAFT

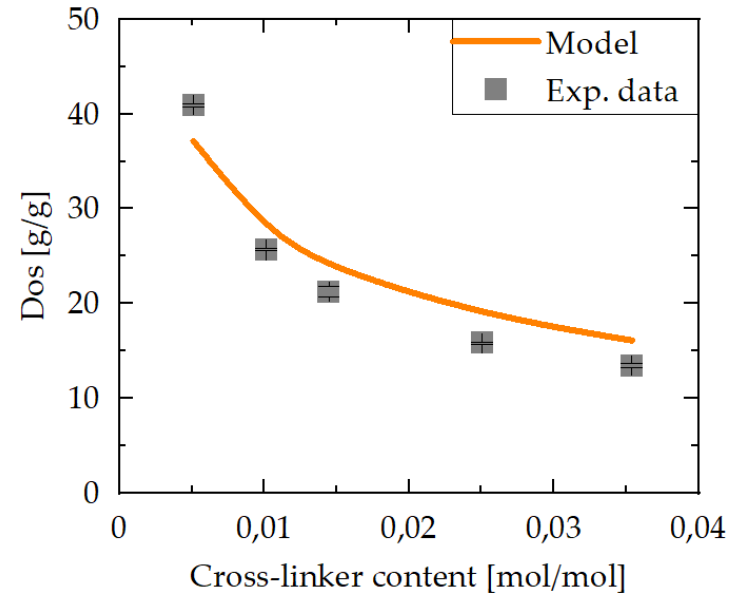
**Degree of swelling (DoS):**

$$DoS = \frac{m_{Gel,eq.}}{m_{pure\ polymer}}$$

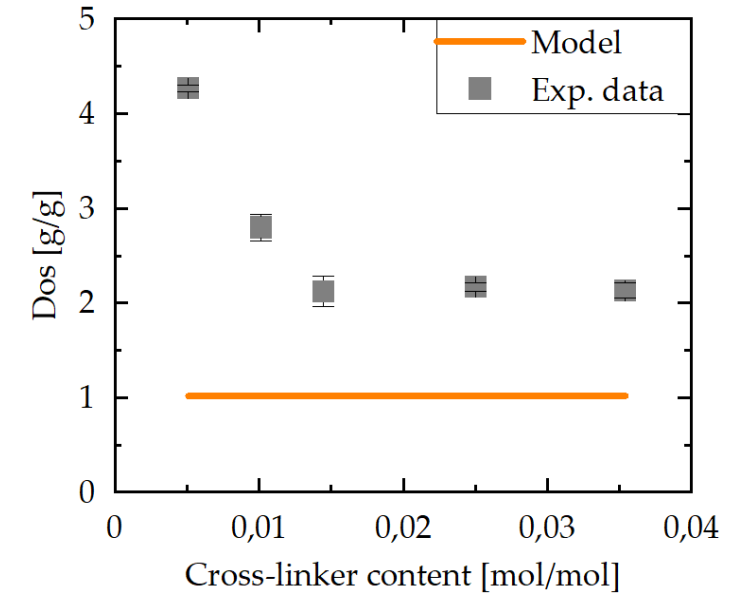
PNIPAAm-Water:



PNIPAAm-Acetic Acid:



PNIPAAm-Butyl acetate:

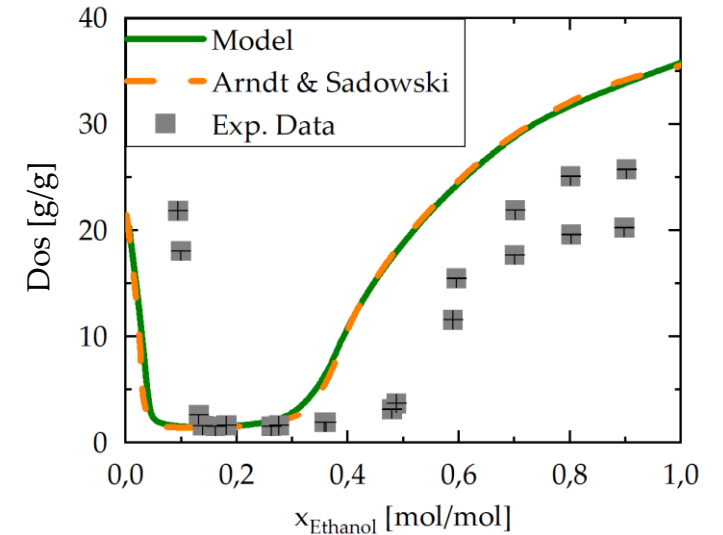
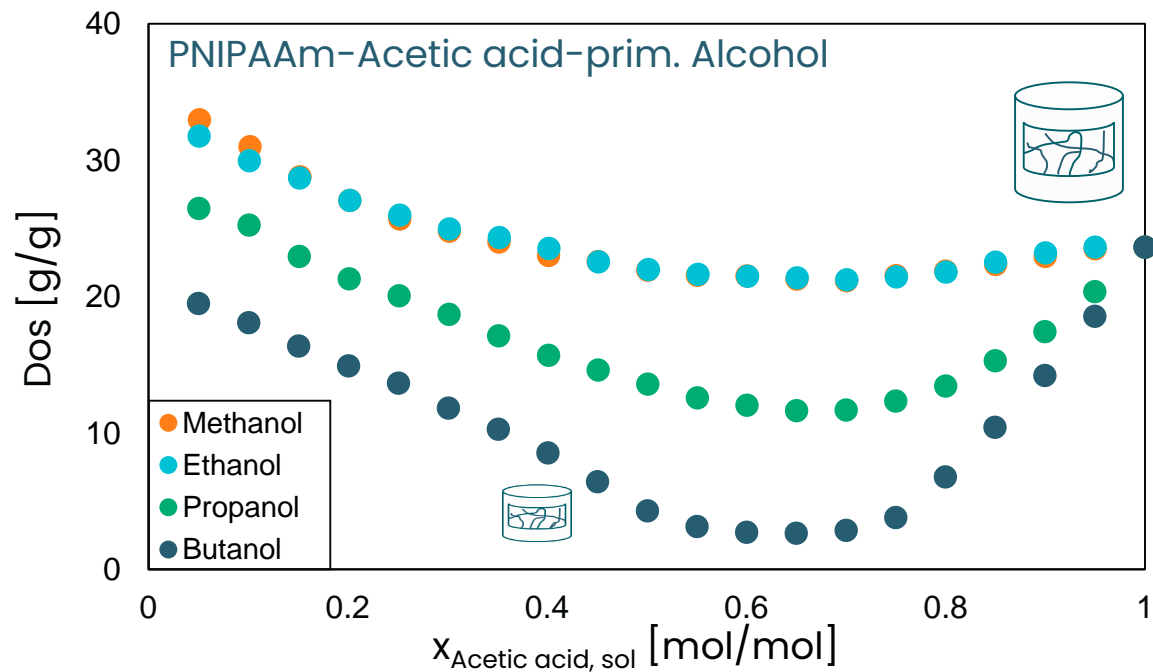


- Swelling behavior depends on hydrophobicity and functional groups
- Modeling with PC-SAFT possible for hydrophilic solvents

**Swelling well described, Shrinkage shows deviations**

# PC-SAFT: Modeling Binary Solvent Mixtures: Cononsolvency Effect

- Low DoS in mixtures of solvents with positive swelling behavior
  - Known example in literature: PNIPAAm-Water-Ethanol
- Influence on the esterification system:
  - Cononsolvency in Alcohol-Acid mixture expected



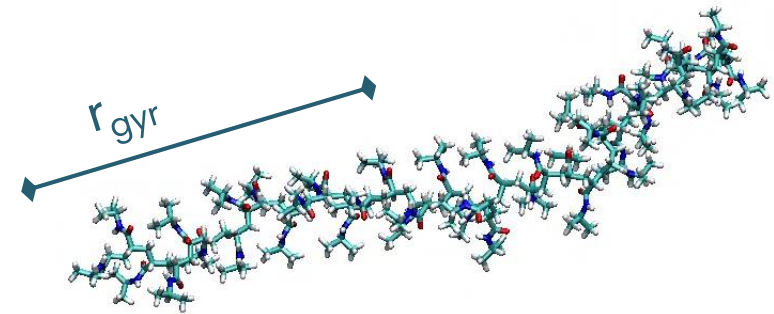
**Magnitude of Cononsolvency effect depends on hydrophobicity.**

➤ **Interactions to be investigated.**

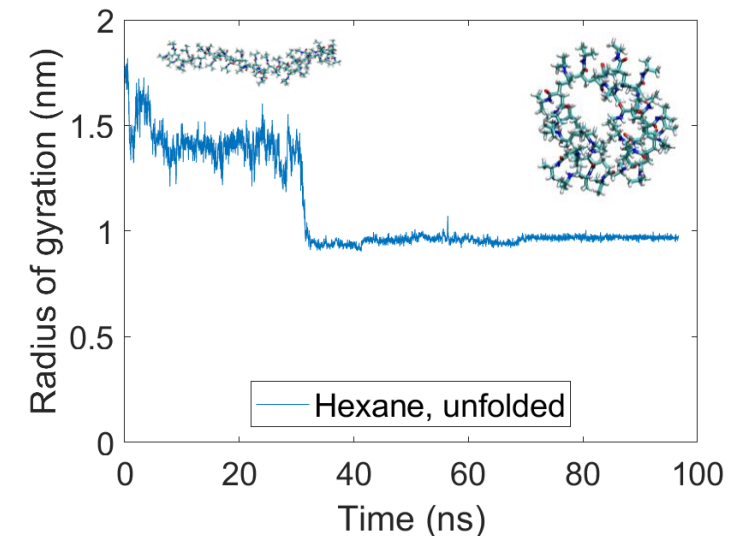
# Additional Modeling Approach: Molecular Dynamic (MD) Simulation

- Linear chain to qualitatively describe behavior
  - Oligomer: 30-40 monomers
  - Folded / open configuration
- Simulations based on calculations of interactions
  - Forcefields of molecules
- Evaluation of results:
  - Radius of gyration (correlated with size)
  - Number of Hydrogen bonds
  - Dynamic analysis over time

**MD enables deeper insights  
in occurring interactions**

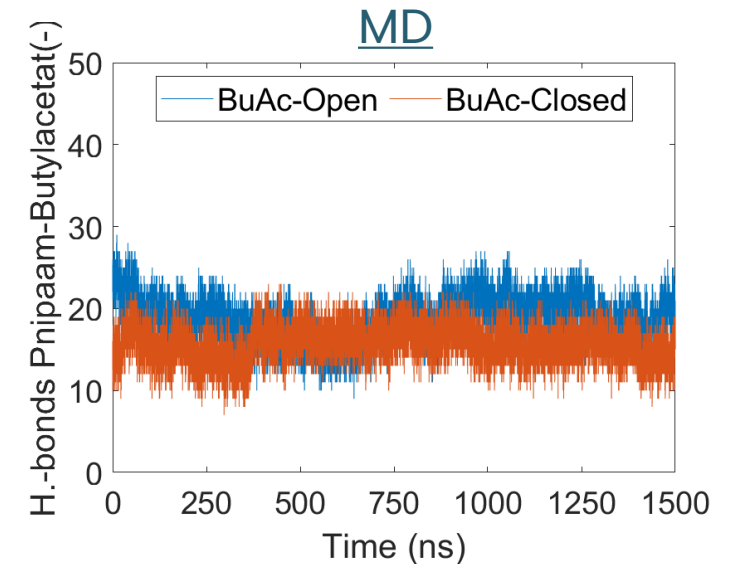
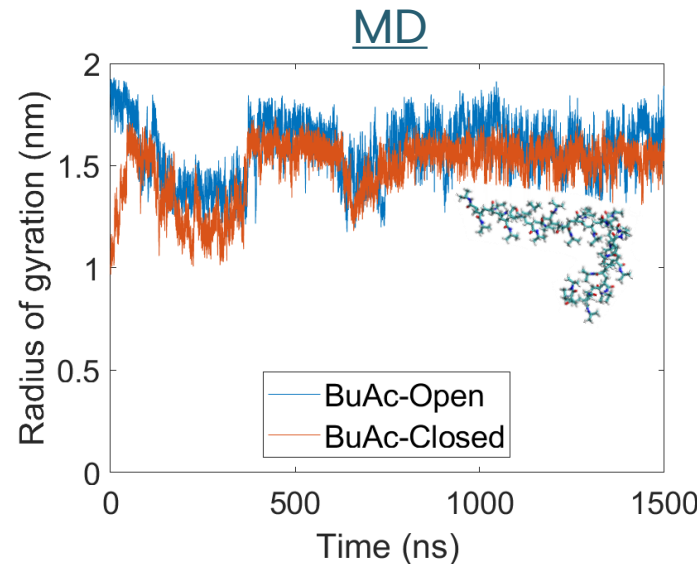
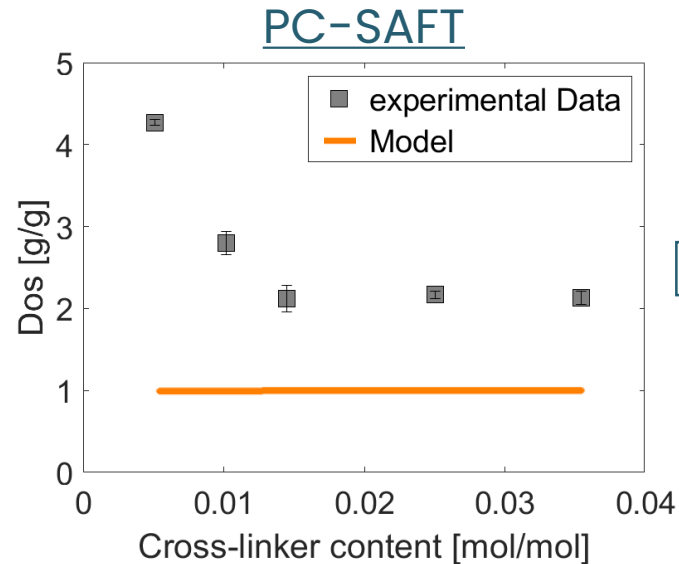


PNiPAAm-Water (40 monomers, 298K)



PNiPAAm-Hexane (30 monomers, 298K)

# MD Simulations of Pure Solvents: Characteristics of Butyl acetate (Ester)

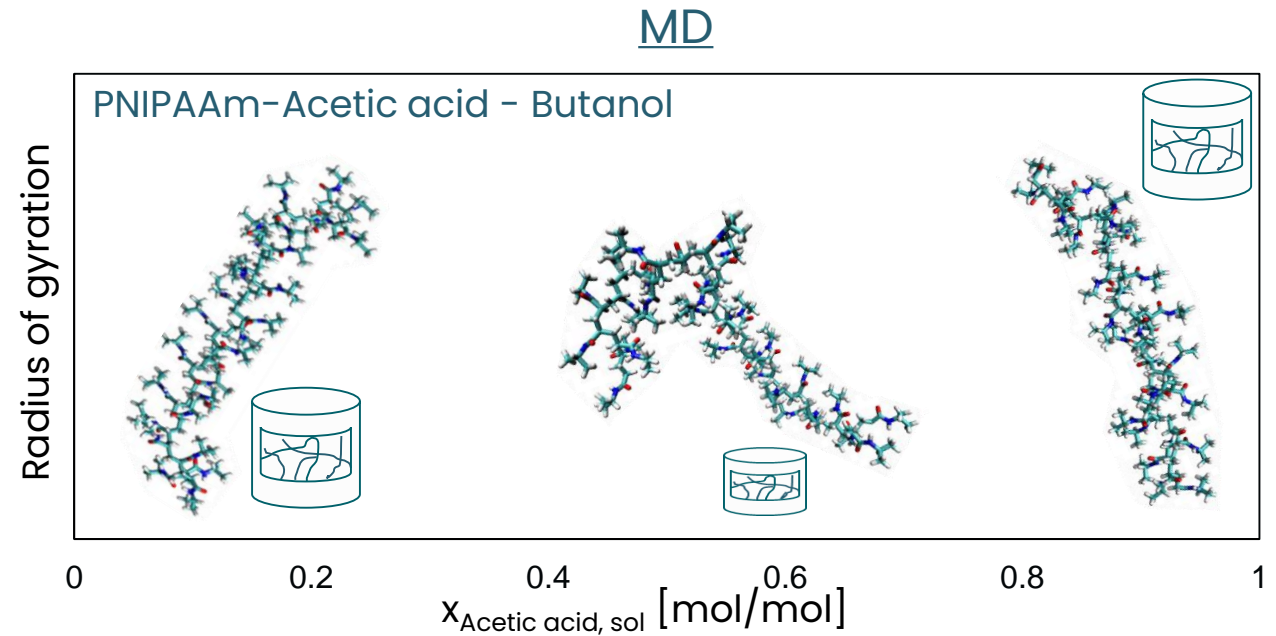
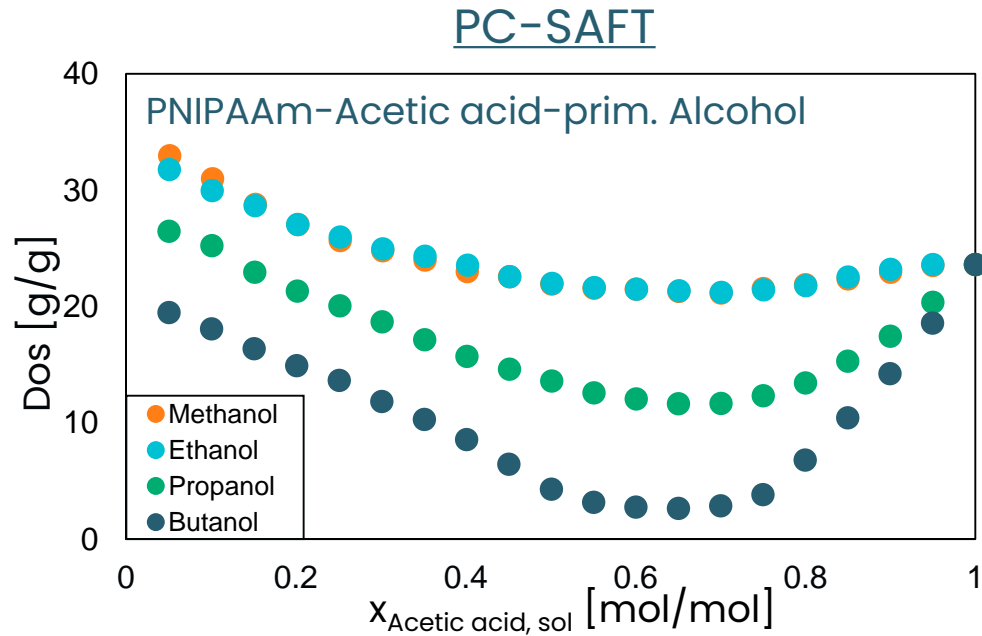


- Experimental data: Low swelling behavior in ester, increasing with low cross-linker amount
- PC-SAFT: Model can not describe behavior

- MD analysis:
  - $r_{gyr}$  refers to larger  $Dos$  as experimental data
  - hydrogen bonds indicate shrinkage

**Distinctive characteristics well predictable.**

# Swelling Behavior in Binary Solvent Mixtures: Acetic acid - Alcohol



- PC-SAFT:

- Prediction of Cononsolvency
- Stronger effect at higher hydrophobicity

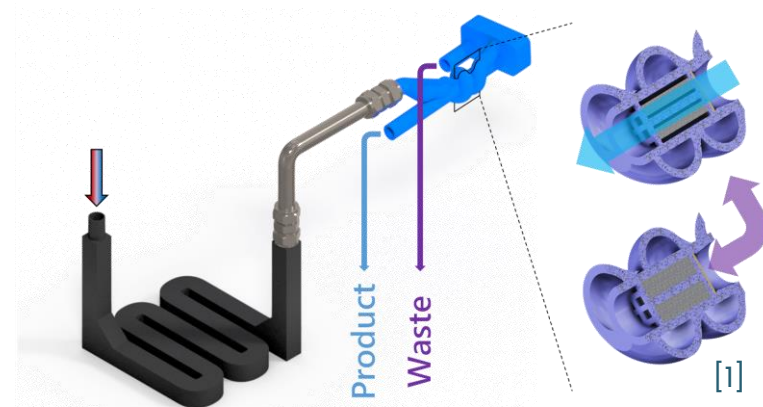
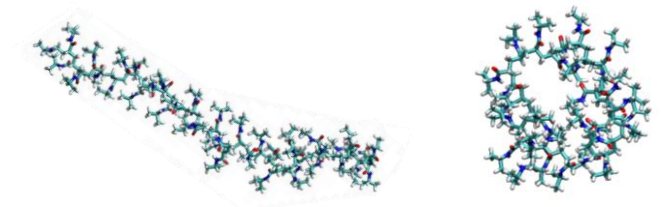
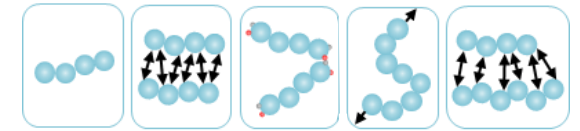
- MD analysis:

- Folded chain in mixtures: Cononsolvency
- Less acid-acid interactions

polymer interactions

**Combination of models enables quantitative & quantitative description.**

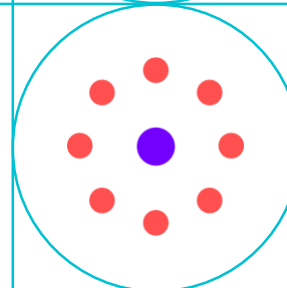
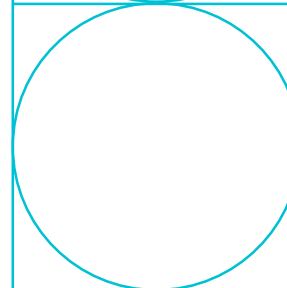
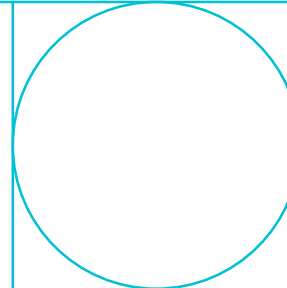
- PC-SAFT: applicable as a tool to calculate degree of swelling
- MD Simulations: qualitative predict interactions and configurations
- Model combination: deeper understanding of occurring interactions
- **Application of responsive gels in smart reactor:**  
Esterification as model reaction
  - Modeling esterification system  
(extension to multi-component systems)
  - Kinetic investigations



# Thank You For Your Attention!

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[tuhh.de](http://tuhh.de)



# TUHH

iCLIMATEBUILT

# Smart Reactors



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