

# Molecular Simulation Study of the Influence of Temperature on the Volume Change of Synthetic Hydrogels

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# Hydrogels

## What is a Hydrogel?

- Three dimensional hydrophilic polymer network
- Swelling (strongly depending on many factors)



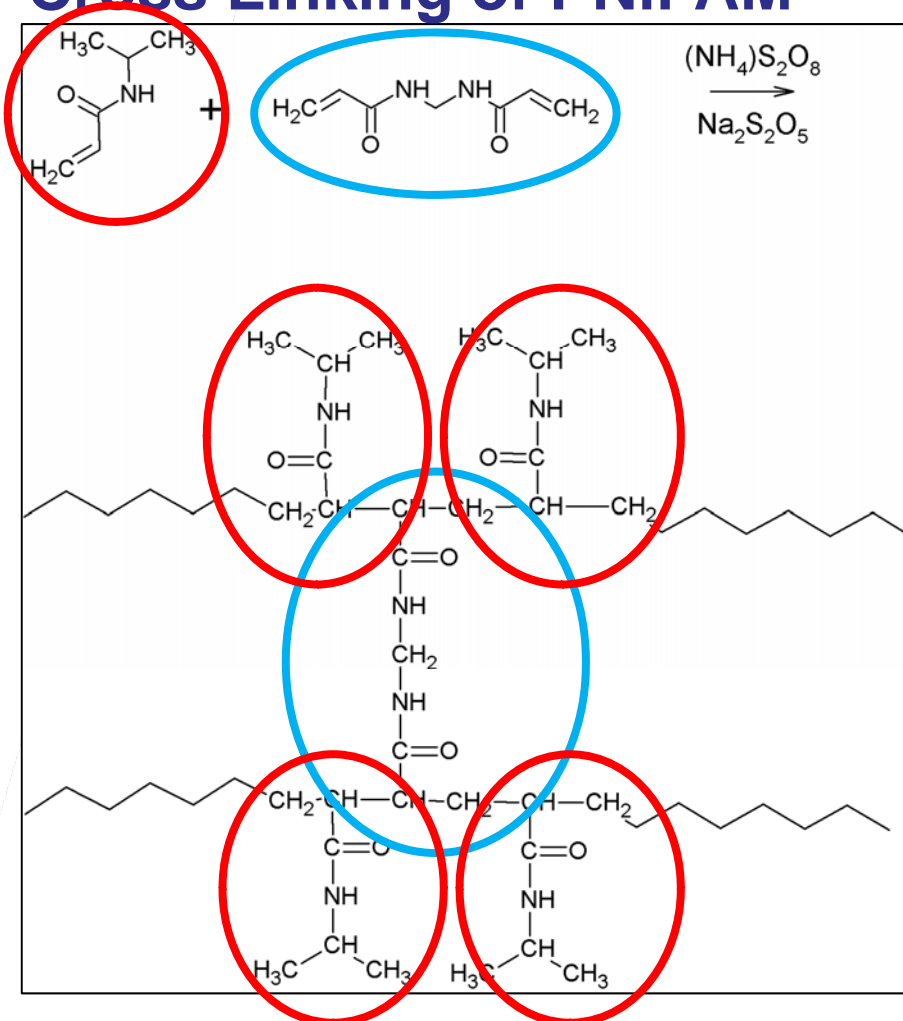
## Examples for Applications:

- Super absorber
- Contact lenses
- Drug delivery systems
- Sensors
- Actors (e.g. micro valves)
- Biocatalysis



# Poly(N-isopropylacrylamide) (PNiPAM)

## Cross Linking of PNiPAM



### Single Chain

- Hydrophilic monomers

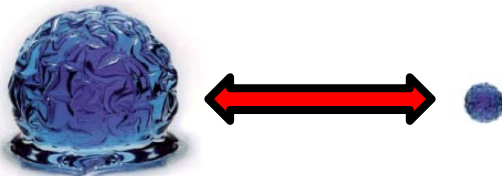
### Cross Linker

- Chemical
- MBA

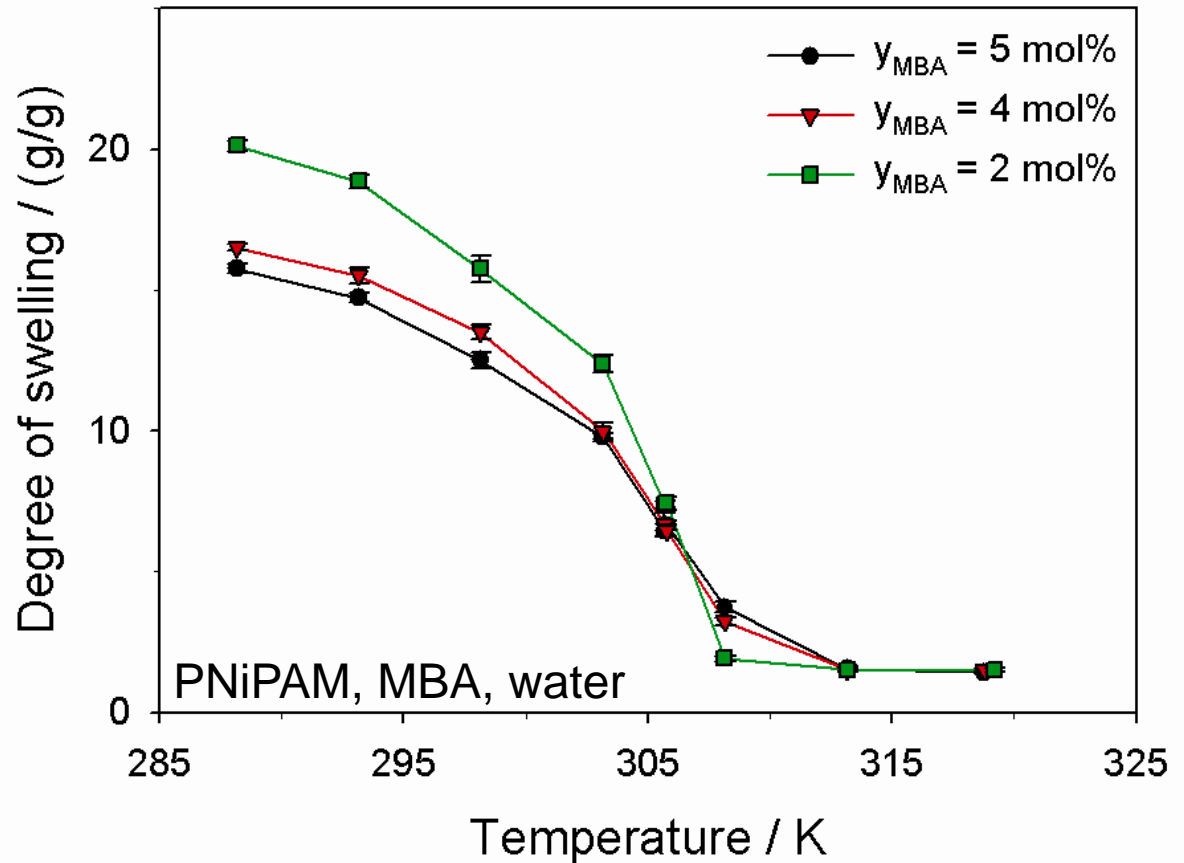
# Degree of swelling in aqueous solutions

## Degree of Swelling depends on:

- Monomer
- Co-monomer(s)
- Cross linker amount
- Solvent
- pH-value
- Salt concentration
- Temperature
- ...



## Influence of the Temperature



# Molecular Modeling and Simulation

## Modeling:

- Force fields from literature

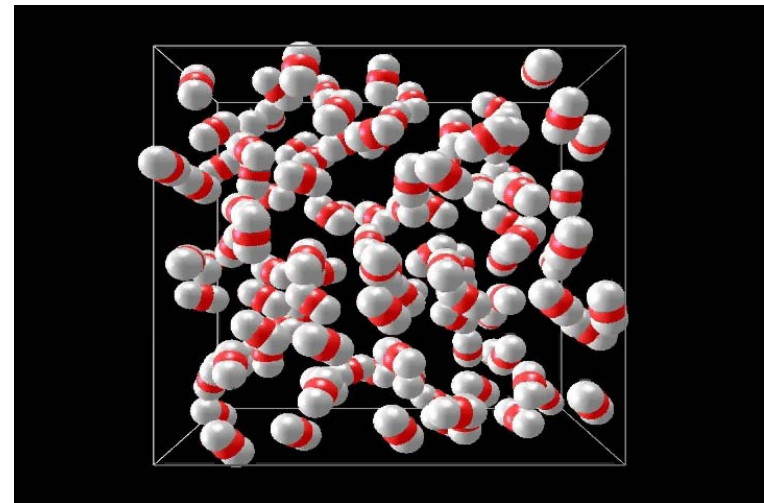
PNiPAM	water: SPC/E	water: TIP4P
Gromos87 UA	✓	✓
Gromos96 53a6 UA	✓	✓
OPLS AA	✓	✓

## Simulation:

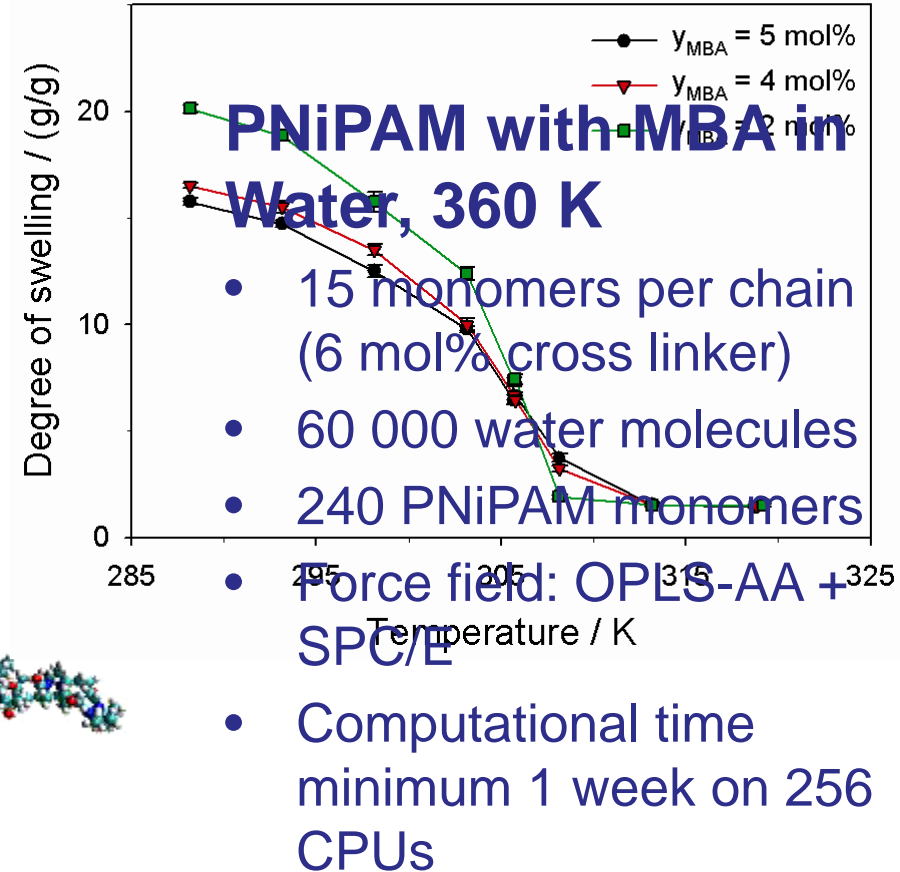
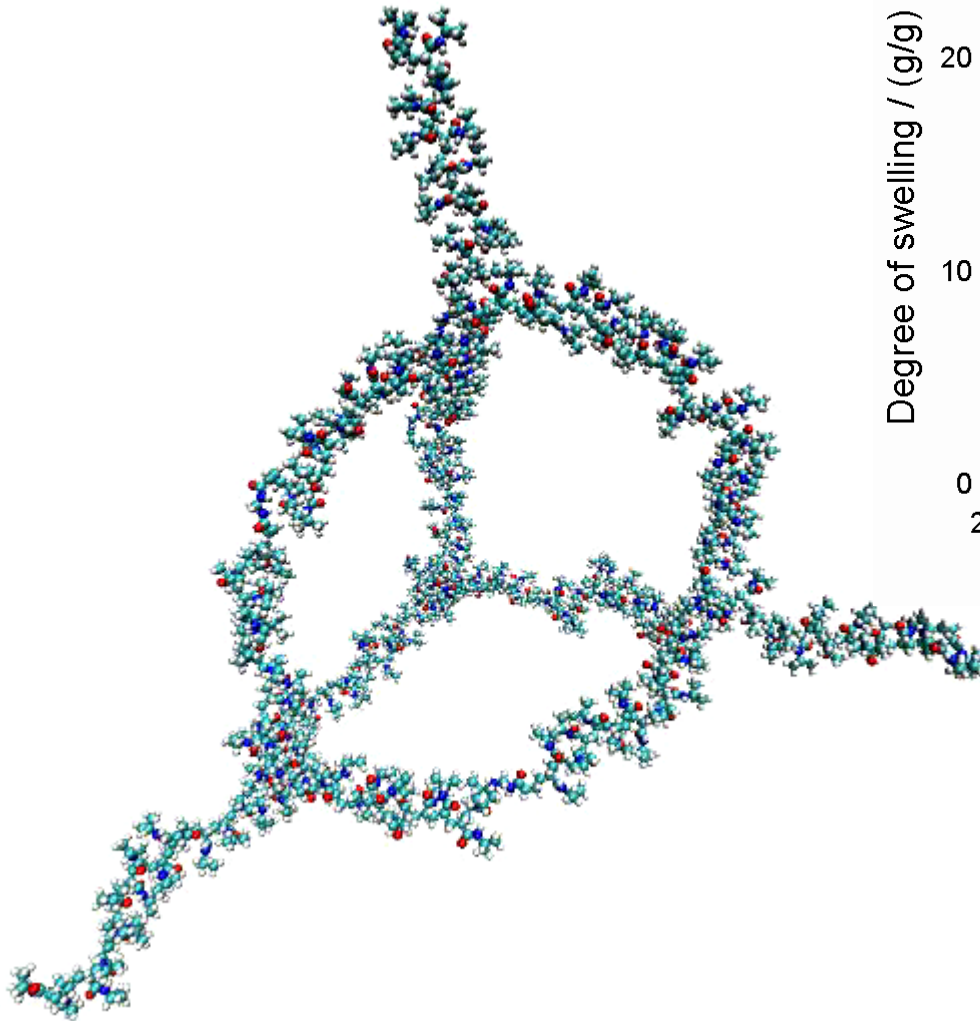
- Molecular dynamics (MD)
  - Newtonian equations of motion
- NpT-ensemble

## Program:

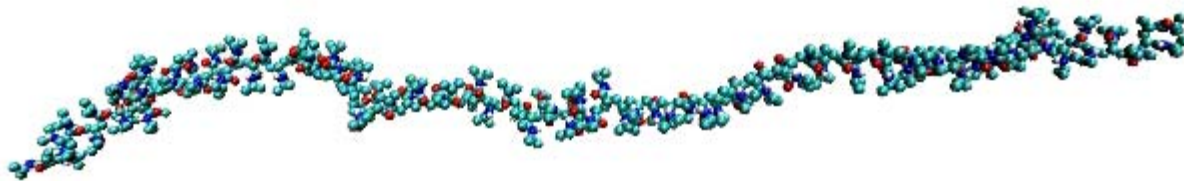
- Gromacs 4.0.x



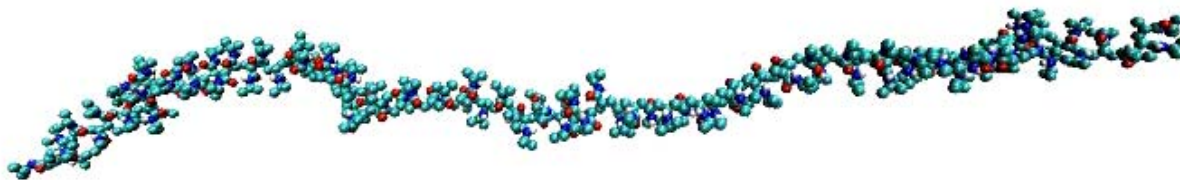
# MD-Simulation Hydrogel Network



# MD-Simulation Single Chain



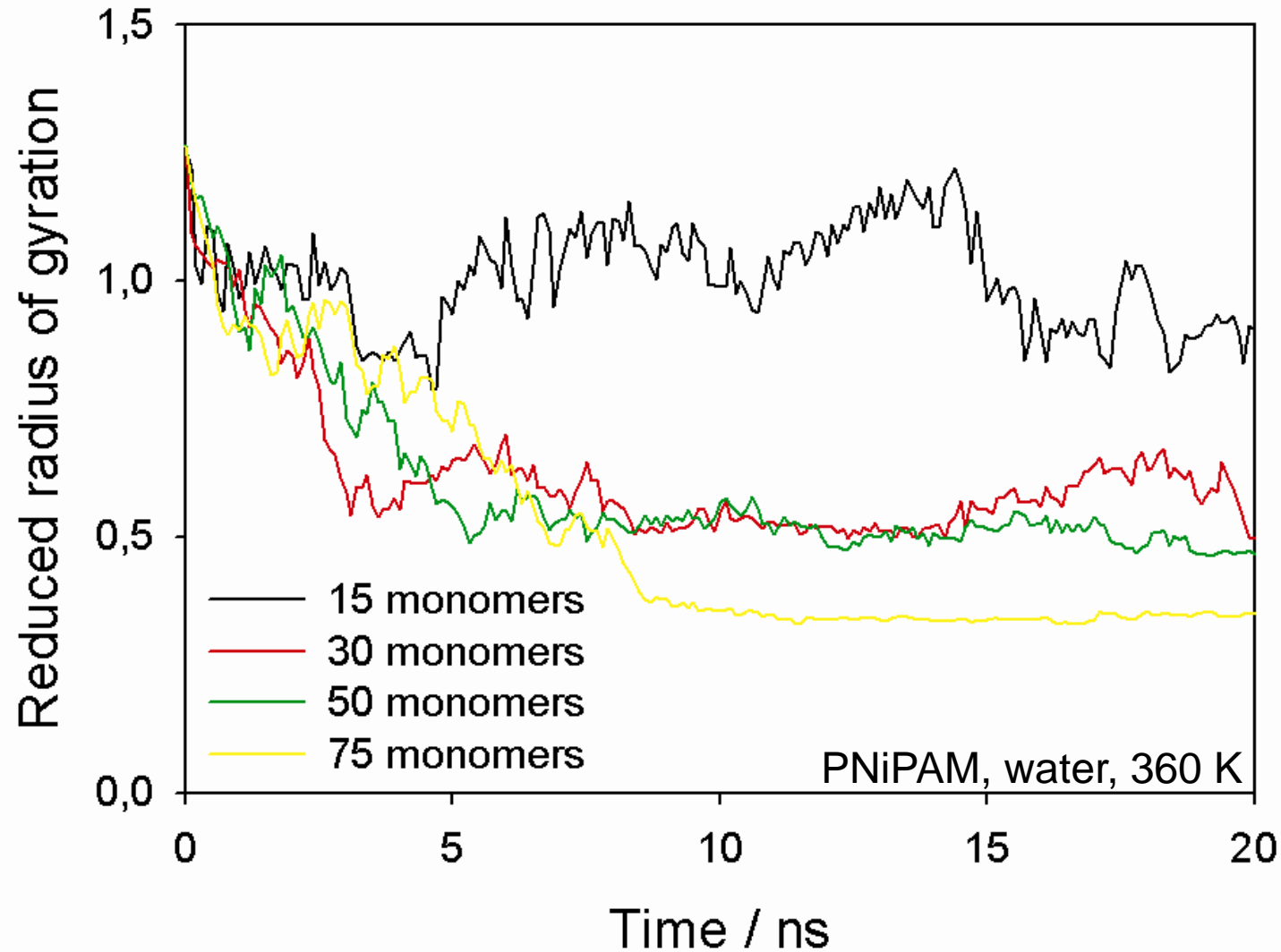
280 K



360 K

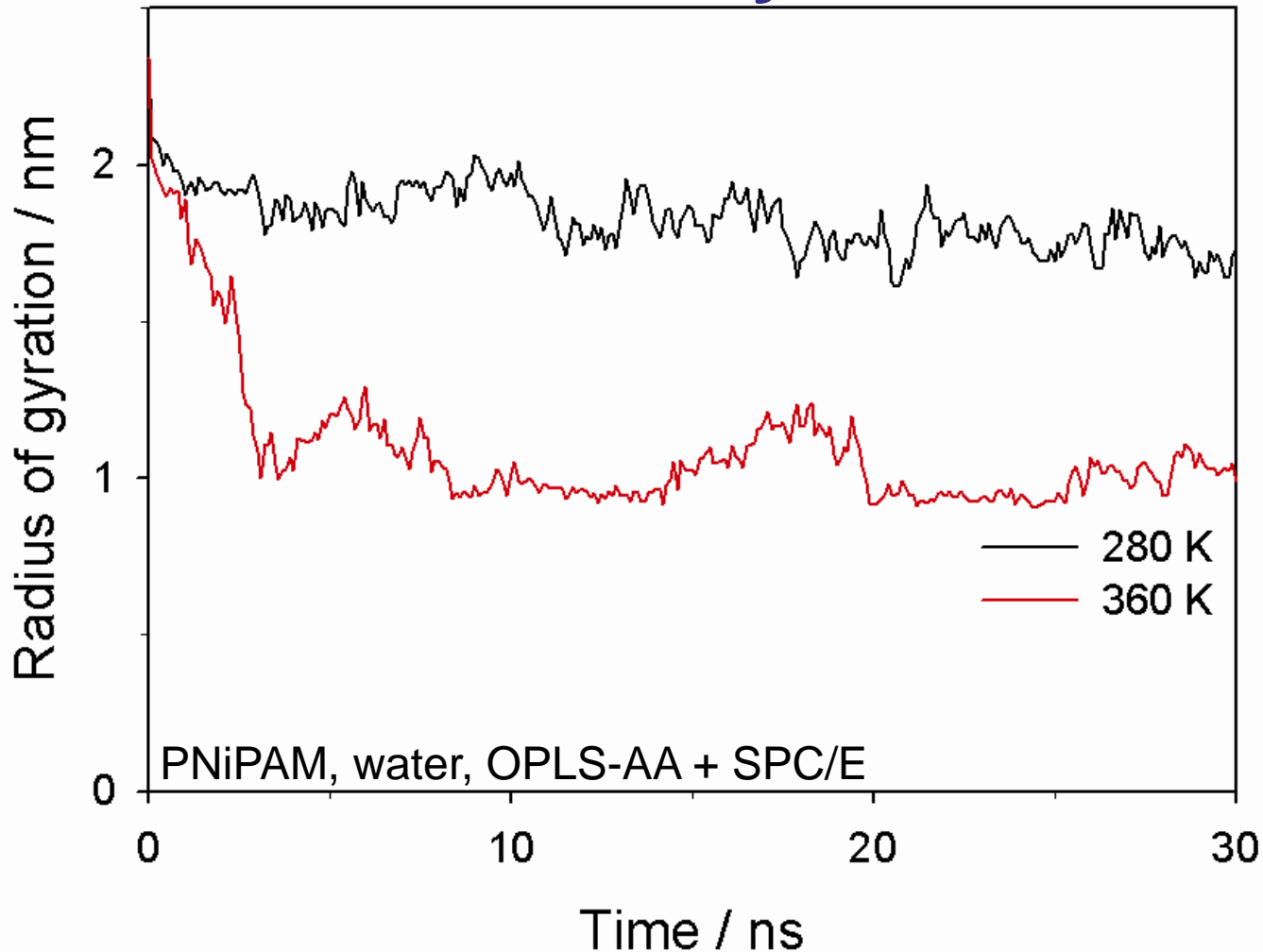
PNiPAM, water, OPLS-AA + SPC/E, 75 monomers

# Preliminary Study: Chain Length

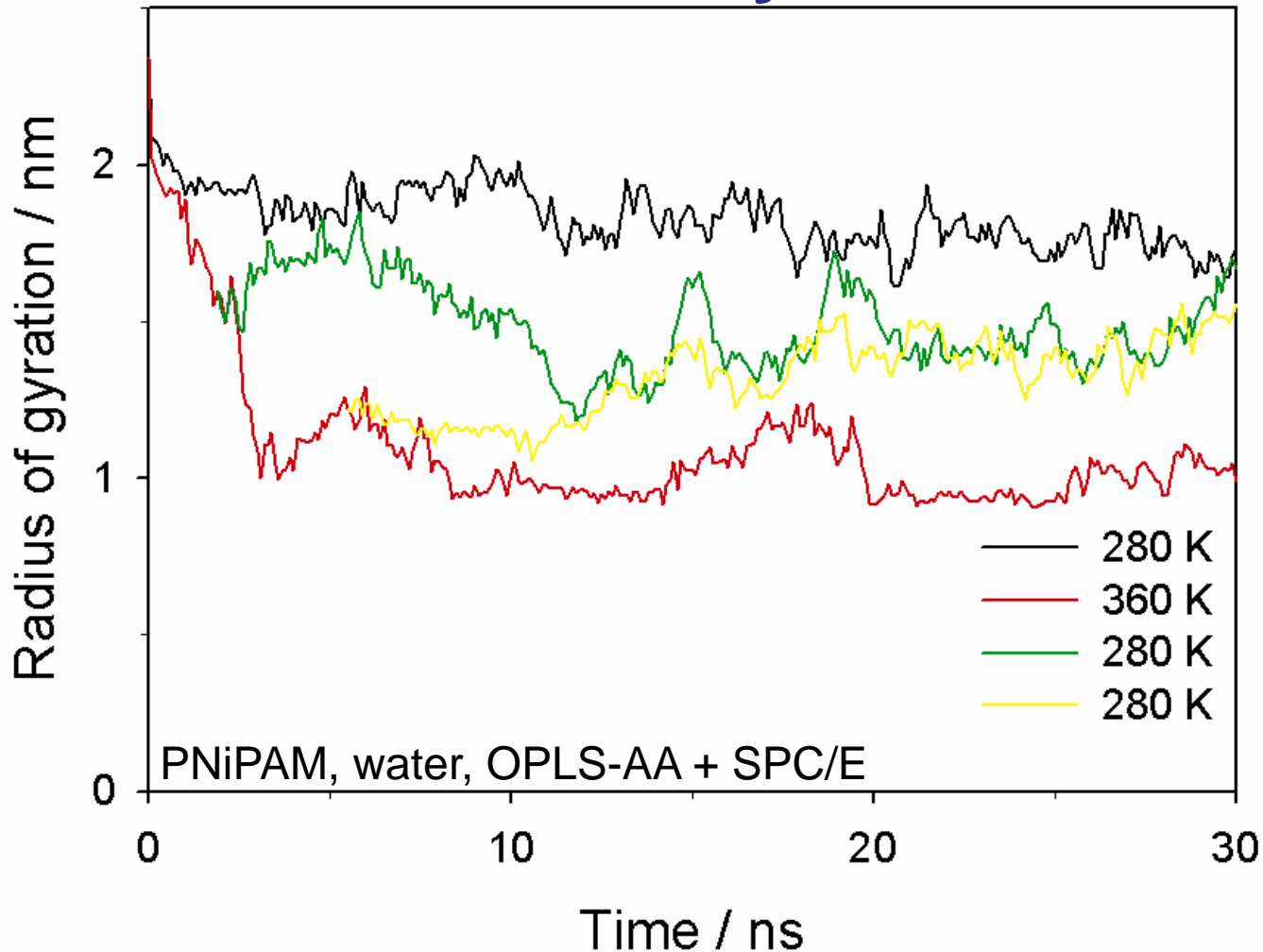




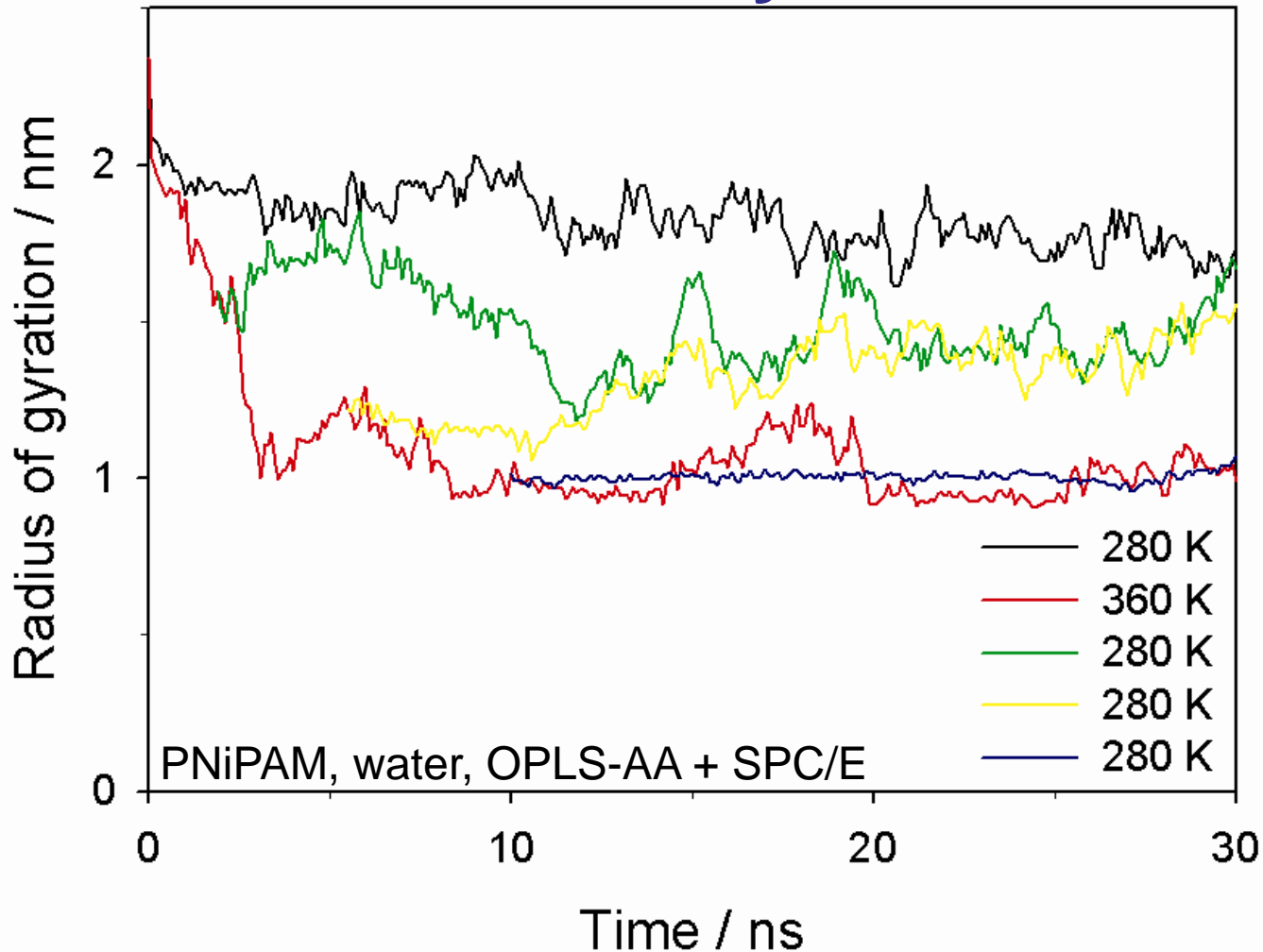
# Temperature Dependence of Single Chain Radius of Gyration



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# Temperature Dependence of Single Chain Radius of Gyration





# Force Field Comparison - Results

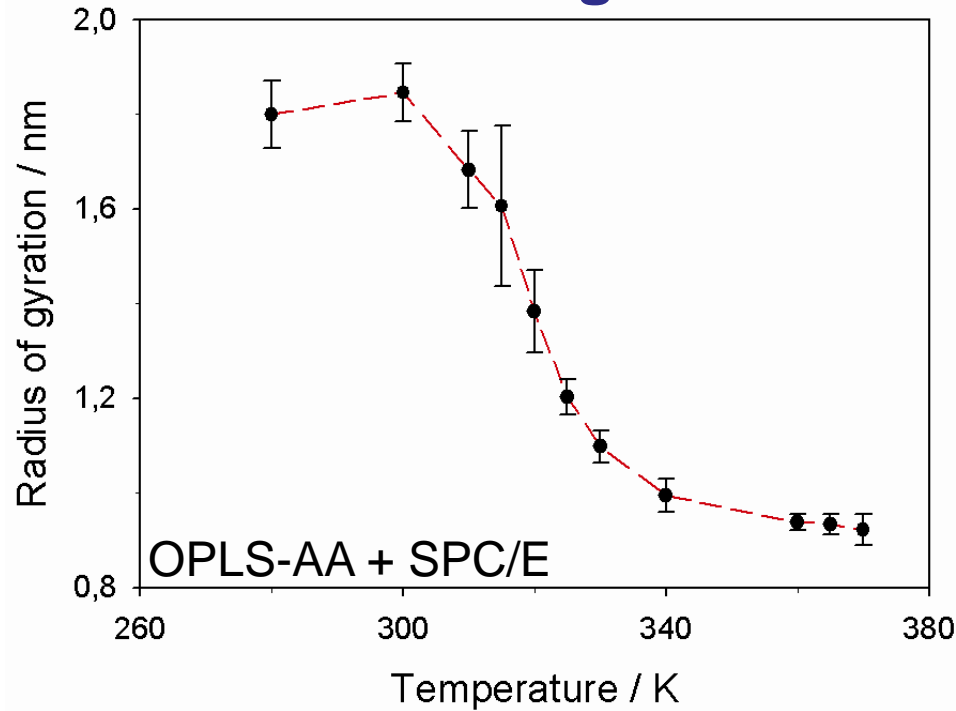
PNiPAM	water: SPC/E	water: TIP4P
Gromos87 UA	-	-
Gromos96 53a6 UA	-	+
OPLS AA	+	+

## Legend

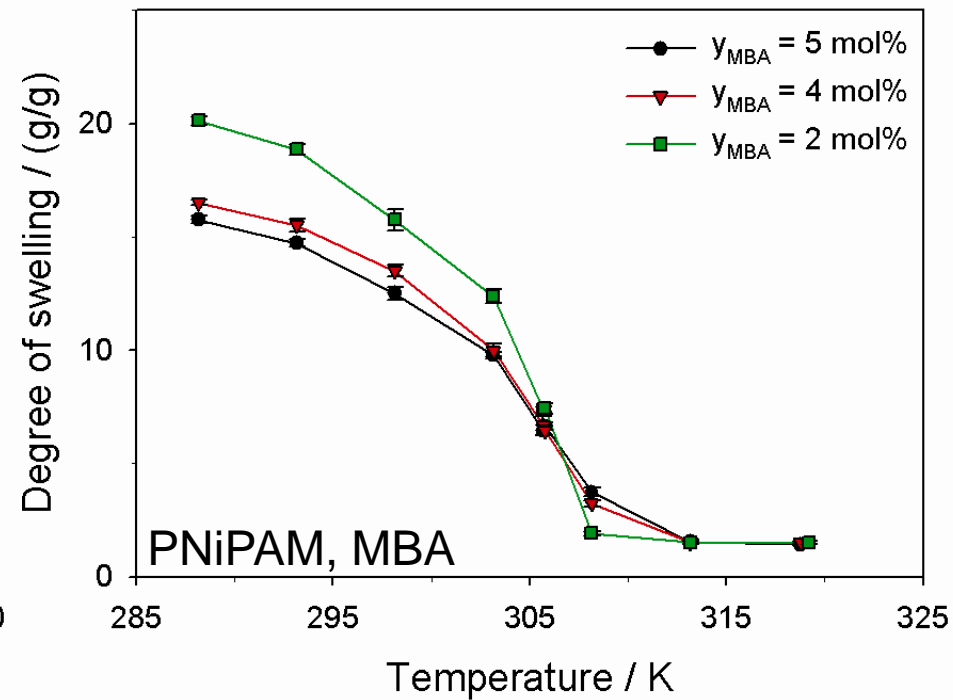
- Force field does not predict effect
- + Force field predicts effect

# Temperature Dependence of the Swelling of PNIPAM in Water

## Simulation Single Chain



## Experiment Hydrogel



# Conclusions

- Swelling of hydrogels: PNiPAM
- Molecular modeling and simulation
- Temperature dependence of swelling
- Hydrogel swelling simulations:
  - Networks
  - Single chains
- Qualitative predictions with force fields from the literature
- Development of force fields for quantitative predictions



**Thanks:**



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**And you for your Attention**