

JCNS DEUTERATION LAB

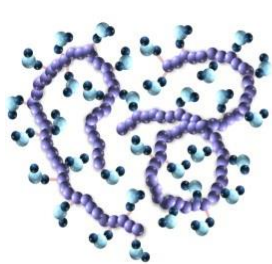
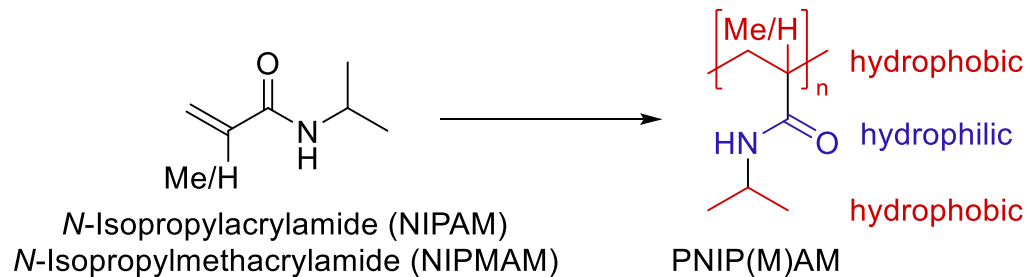
Deuterated Acryl- and Methacrylamides as Monomers for
Thermoresponsive Polymers

22ND MARCH 2023

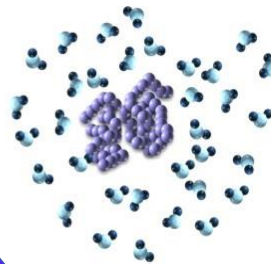
DR. KUNO SCHWÄRZER



THERMORESPONSIVE POLYACRYL- AND POLYMETHACRYLAMIDES



Hydrophilic coils

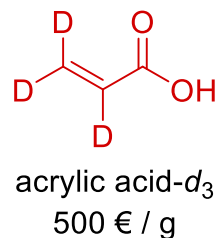
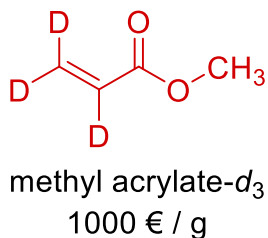
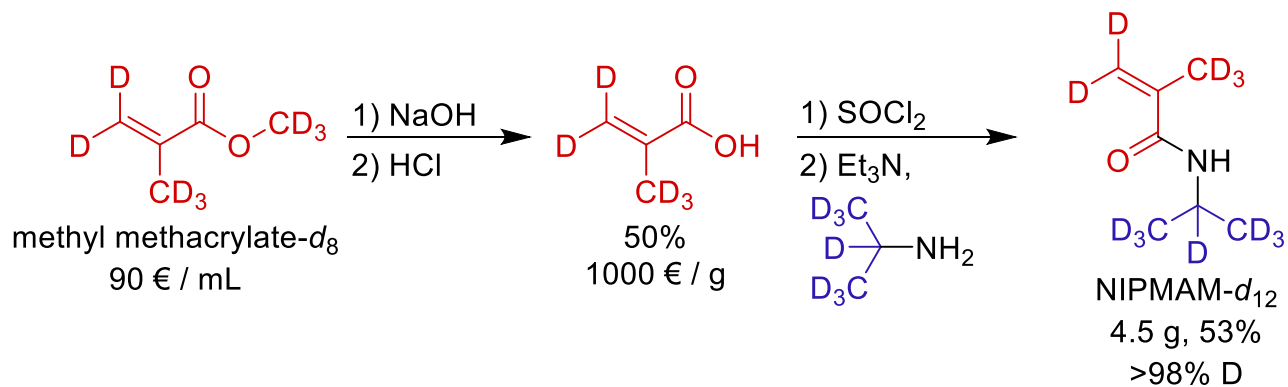
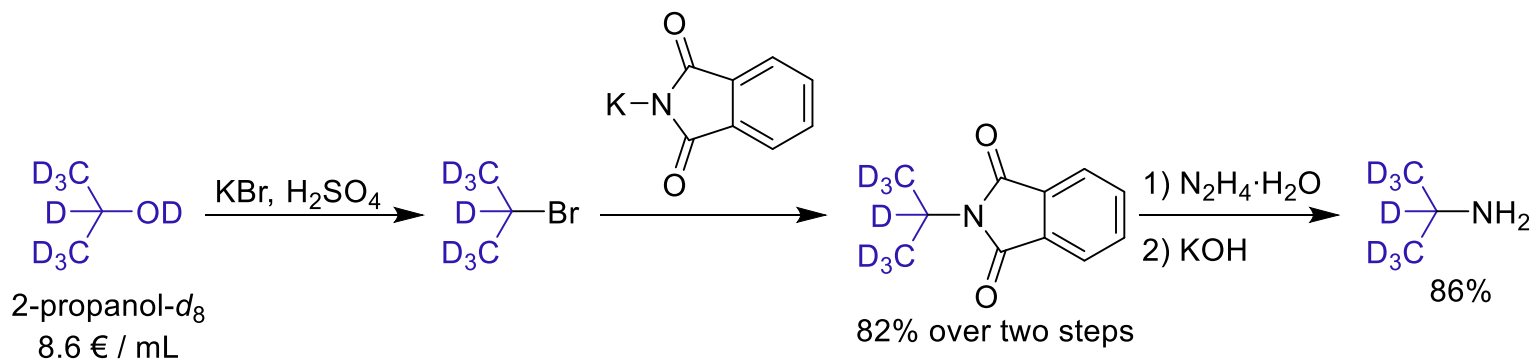


Hydrophobic globules

Lower Critical Solution Temperature
(LCST) $\approx 32\text{ }^{\circ}\text{C}$

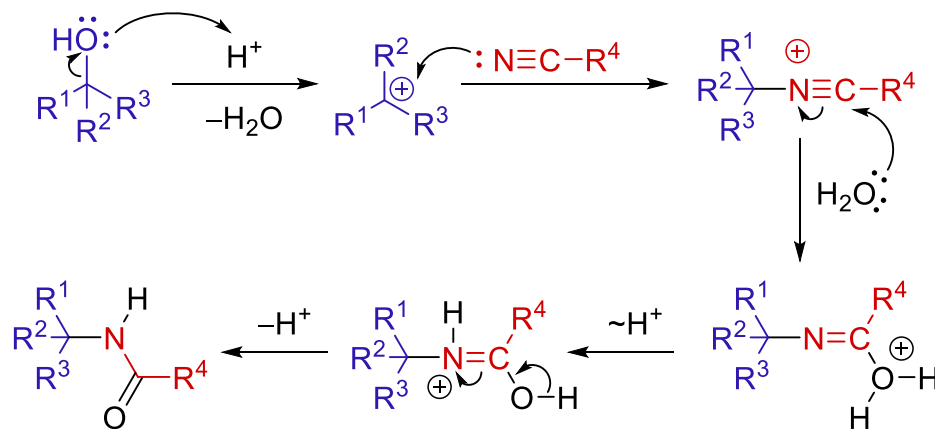
- Temperature and pH sensitive drug delivery systems
- Macroscopic gels and microgels converting external stimuli into mechanical motion
- Thin films as nano-switches

SYNTHESIS OF NIPMAM- d_{12}

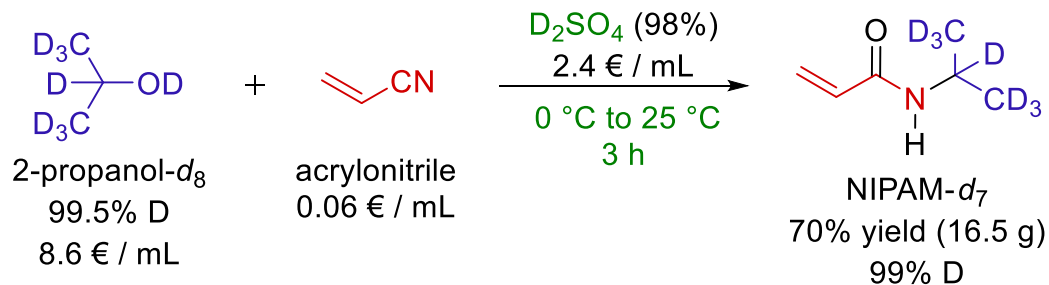
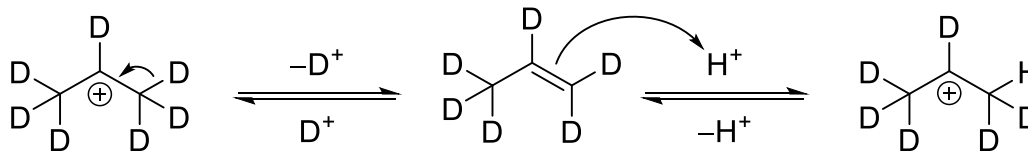
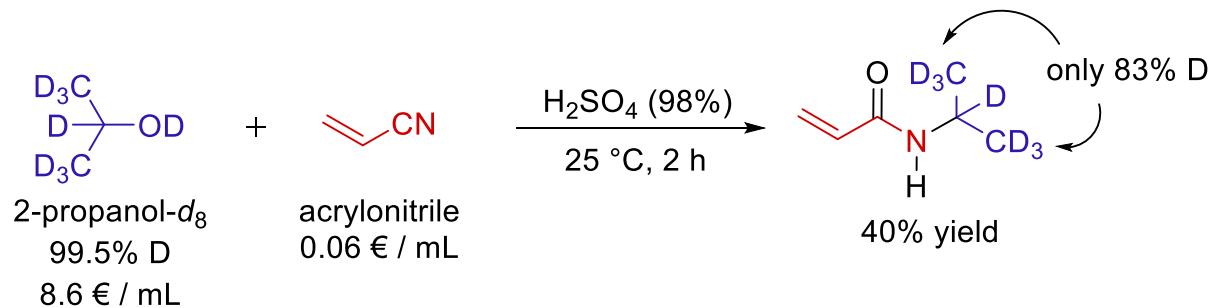


NEW SYNTHETIC APPROACH: THE RITTER REACTION

- Conversion of nitriles into *N*-alkyl amides via carbocations
- First reported by J. Ritter and P. Minieri in 1948
- Most commonly utilizes tertiary or benzylic alcohols



SYNTHESIS OF NIPAM- d_7



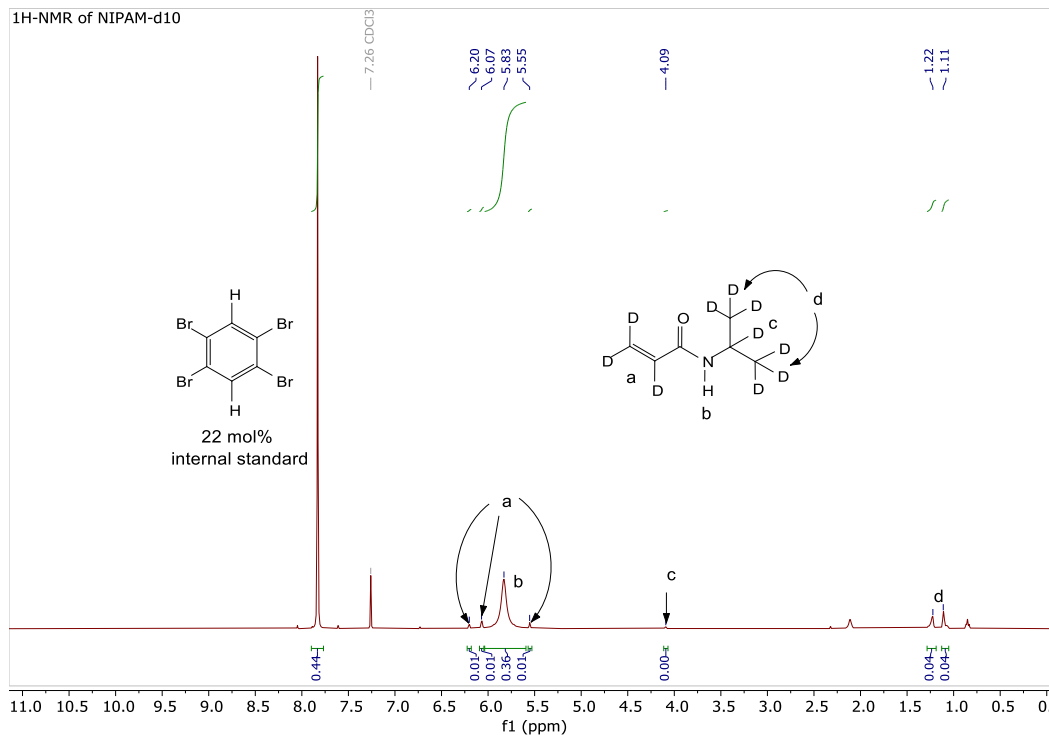
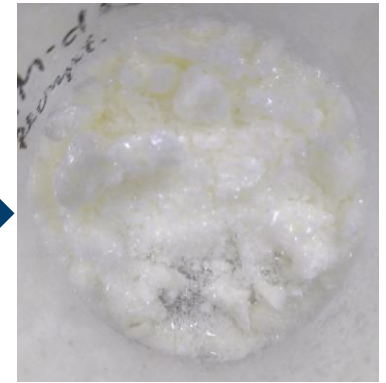
Material cost: <500 €

Commercial Price:
10000 €

PURIFICATION

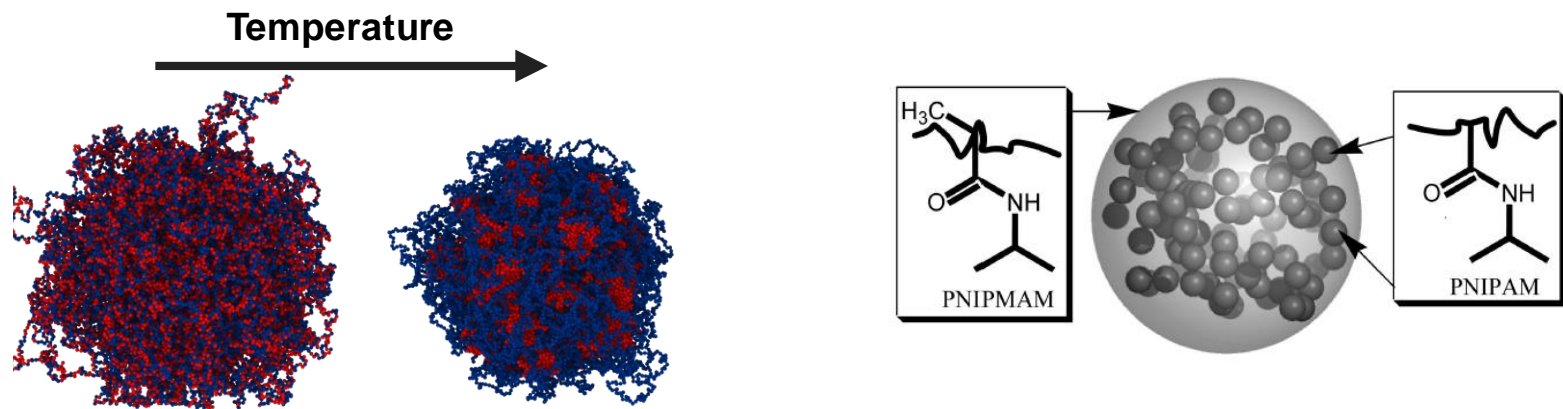


Recrystallization



LINK BETWEEN INTERNAL STRUCTURE AND VPTT OF PNIPAM-PNIPMAM MICROGELS

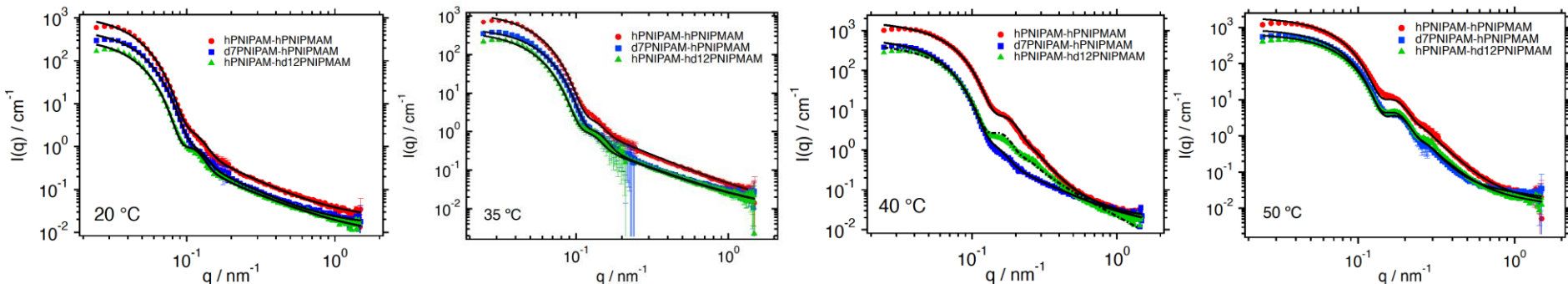
- Fine tuning of the volume phase transition temperature (VPTT) of microgels by mixing PNIPAM-PNIPMAM
- Detailed understanding of the effects of copolymerization on the internal morphology of microgels is still missing
- Preliminary experiments and simulations suggest nanophase separation close to the VPTT



Keerl *et. al.*, *JACS* **2009**, 131, 3093.

LINK BETWEEN INTERNAL STRUCTURE AND VPTT OF PNIPAM-PNIPMAM MICROGELS

- Preparation of 3 PNIPAM-PNIPMAM (50:50) microgels: (h)PNIPAM-(h)PNIPMAM, (d7)PNIPAM-(h)PNIPMAM and (h)PNIPAM-(hd12)PNIPMAM (VPTT = 38.3-42.5 °C)
- Analysis via small angle scattering, simulations and super-resolution microscopy
- Partial deuterium labelling of either PNIPAM or PNIPMAM to change the contrast



- Compaction of the form factors at higher T due to characteristic microgel deswelling
- At 20 °C and 50 °C all form factors present closely comparable shapes
- Significant differences at 35 °C and especially 40 °C with extra scattering at $q > 0.2 \text{ nm}^{-1}$ could be connected to the expected inhomogeneous distribution of the polymers

JCNS DEUTERATION SERVICE

Second call for deuteration proposals currently open on the MLZ conference hosting platform indico:

<https://indico.frm2.tum.de/e/deuteration2>

Deadline: 31st of May 2023



Please contact deuterierung@fz-juelich.de before submitting your proposals

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- Jürgen Allgaier
- Benedetta Rosi
- Claas Hövelmann
- Marco Laurati
- Gavino Bassu
- Emanuela Zaccarelli
- Francesco Brasili



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