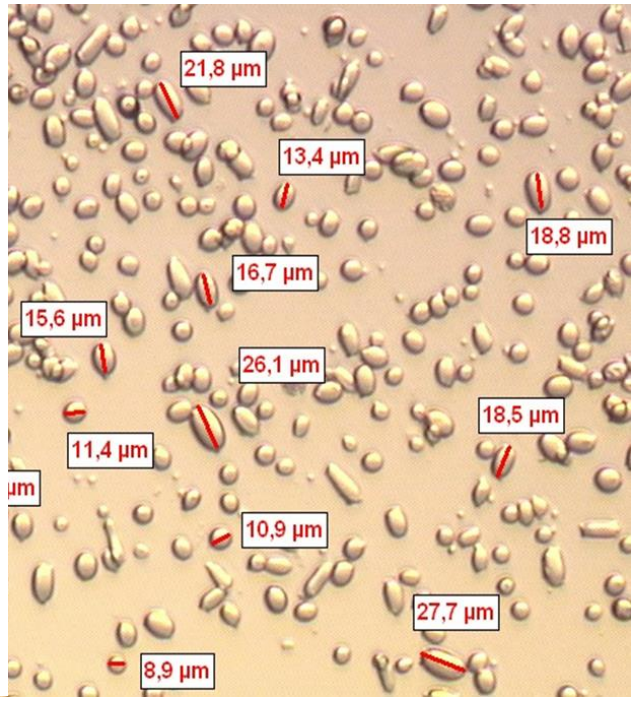
SYNTHESIS OF CATIONIC POLYELECTROLYTES BY DISPERSION POLYMERIZATION IN AQUEOUS ALUMINUM SALT SOLUTIONS

Antje Lieske; Fraunhofer Institute for Applied Polymer Research IAP; Potsdam-Golm



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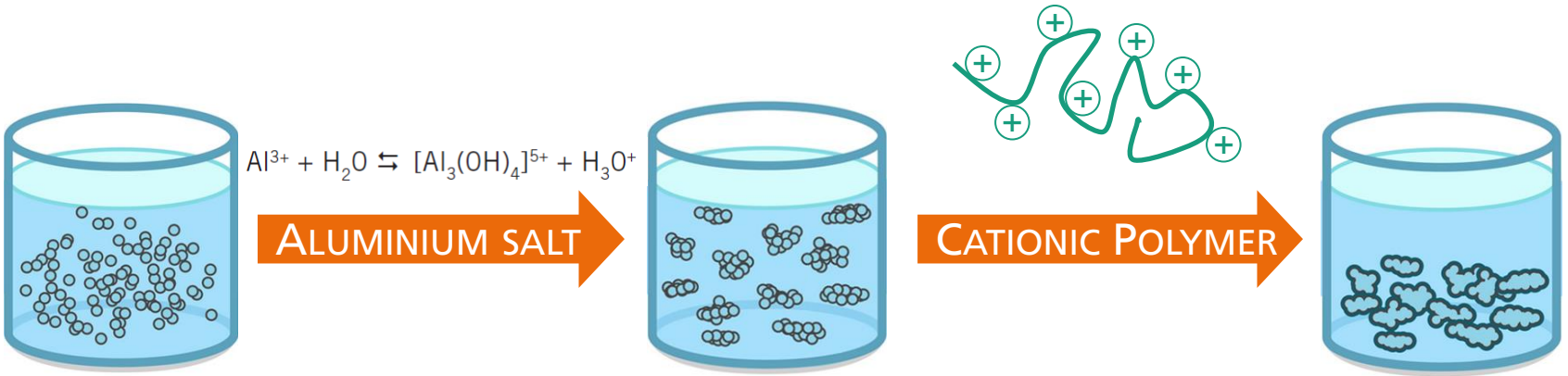
SYNTHESIS OF CATIONIC POLYELECTROLYTES BY DISPERSION POLYMERIZATION IN AQUEOUS ALUMINUM SALT SOLUTIONS

- The Story Behind
- Process Development and Results
- Application Tests
- Summary

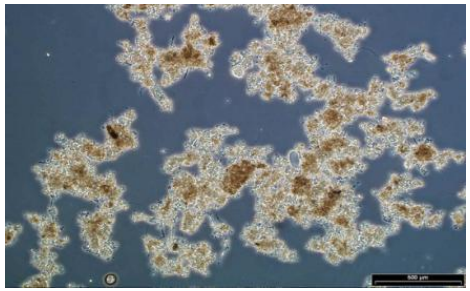
Flocculation Aids

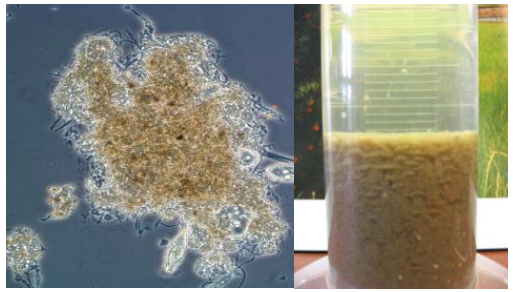
- High molecular weight cationic polyelectrolytes are used in waste water treatment, sludge dewatering and paper making
- How does it work?



MICROFLOCS

MACROFLOCS





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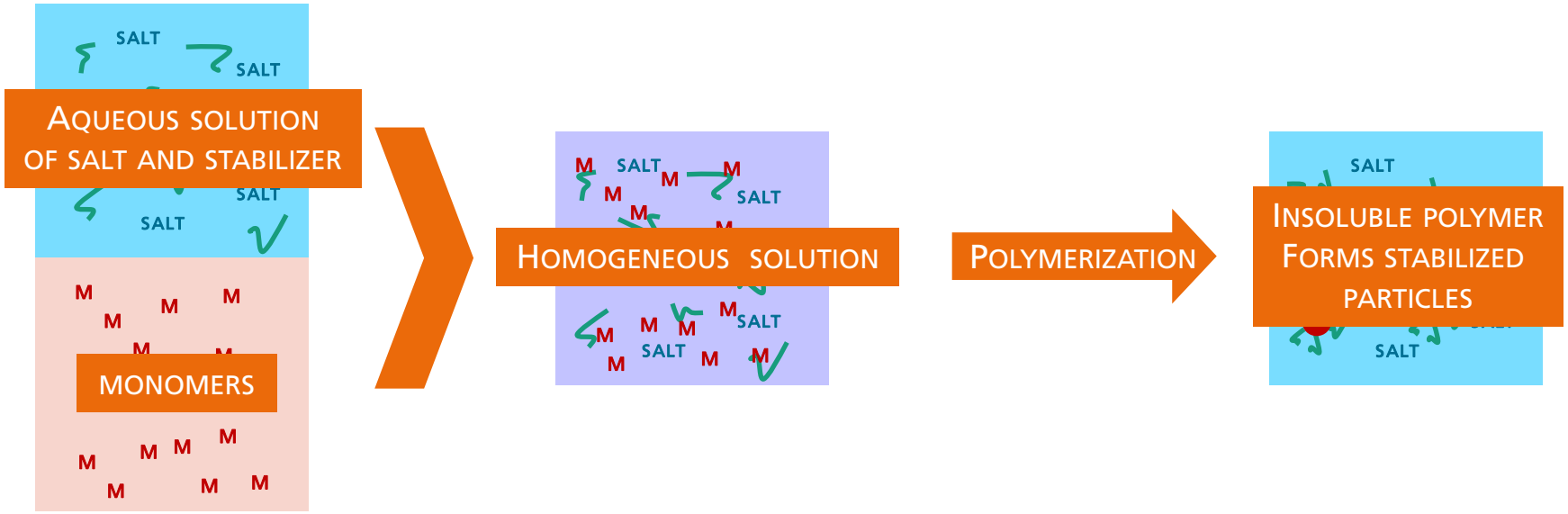
Synthesis of cationic polymer

- Mostly copolymers of acrylamide and cationic acrylic esters
- Polymerisation in solution (technically on conveyor belts)
  - Easy
  - Molecular weight limited
  - Has to be dried and cutted
- Inverse emulsion polymerization
  - Highest molecular weight, good control of heat removal and viscosity
  - Contains oil and surfactants, has to be inverted
- Aqueous dispersion polymerization
  - Good control of heat removal and viscosity, readily soluble
  - Contains salts (inorganic or low molecular weight polyelectrolytes)

AQUEOUS DISPERSION POLYMERIZATION



- PROJECT IDEA DRIVEN BY SMALL COMPANY, PRODUCER OF ALUM AND PAC
- REPLACE THE SALT IN AQUEOUS DISPERSION POLYMERIZATION BY ALUM/PAC?
  - COMBINATION OF FLOCCULANT AND FLOCCULATION AID
  - ONE DOSAGE STREAM INSTEAD OF TWO
  - NO INTERFERING SALTS

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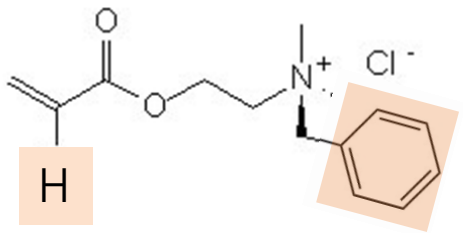
Preliminary investigations

- Basic requirement: adjust salt concentration to keep monomers soluble but render polymers insoluble
  - possible with aluminium salts?? (Mixtures of alum and PAC were to be used)

- synthesis of model polymers from acrylamide and cationic acrylates with varying charge densities



MADAMBQ: R= CH ; R*=Benzyl

Copolymers of AA and these monomers can be precipitated in aqueous NH_4Cl / $(NH_4)_2SO_4$

ADAMMQ: R=H; R*= CH_3

- Yes, it works with aluminium!
- Only hydrophobic BQ-structures can be precipitated by Al salt (no MQ)
- Acrylate copolymers can be precipitated at lower salt concentrations than methacrylate copolymers (equal charge density)
- The lower the charge density the higher the necessary salt concentration

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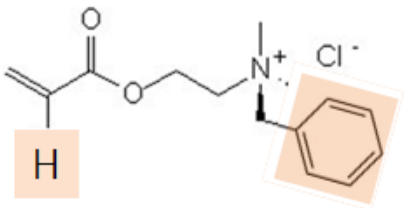
Start conditions for process development



- ADAMBQ as the cationic comonomer (ADAMQUAT BZ80)
- Charge density 30%: medium charge density for flocculation aids
- Polymer content: 20% (20-30% state of the art for ammonium salts)
- Starting salt concentration: 20% $Al_2(SO_4)_3$; 4% PAC

→ Development of initiator system and dosage

→ Development of stabilizer system

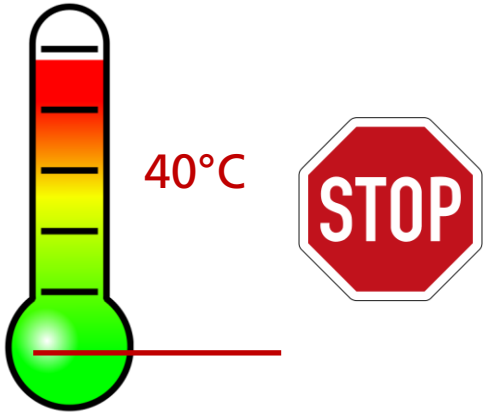
→ Variation of charge density and active content

Initiator system

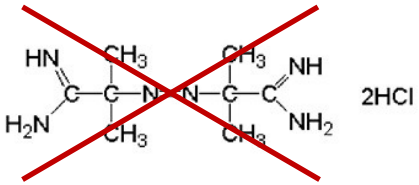
- Since nothing is known about suitable stabilizers, these first experiments were run without stabilizer

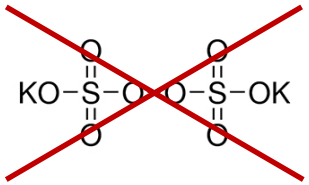
- Gives highly viscous dispersions at high conversion, but OK as starting point

- Solubility of resulting polymer increases markedly with temperature



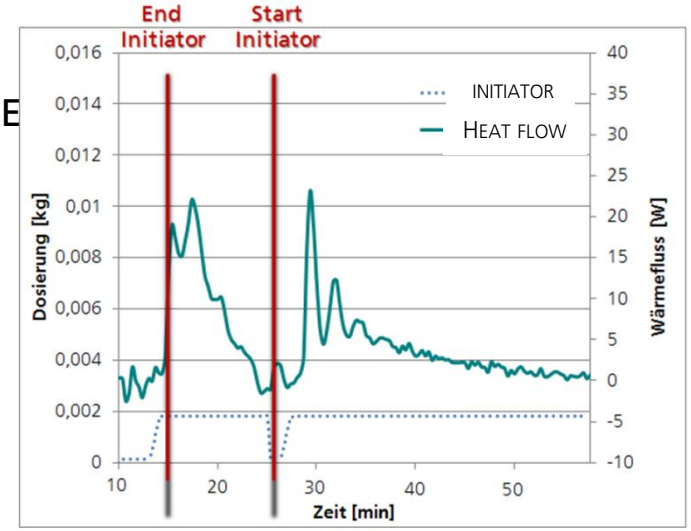
Thermal initiation



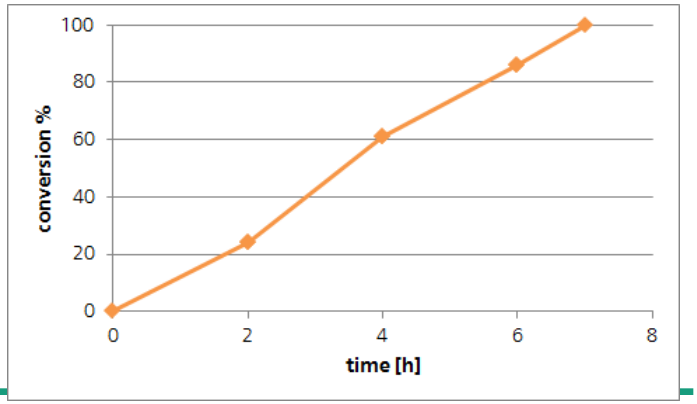


Initiator system

- Redox system ascorbic acid / Fe(II) / persulfate
  - Works at 40°C
  - Very short half life time
  - Dosage has to be developed
    - high molecular weight (low flux of radicals)
    - complete conversion in moderate time
    - uniform conversion over time (no heat peaks)



- Dosage of persulfate was optimized:
  - 100% conversion in 7h, uniform development
  - Molecular weight ~ 5 mio g/mol (SLS)



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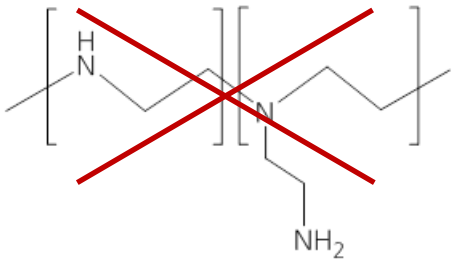
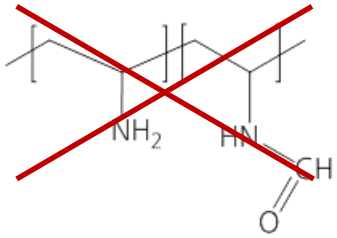
COMMERCIAL CATIONIC POLYMERS AS STABILIZERS

- CATIONIC POLYMERS WITH DIFFERENT STRUCTURES

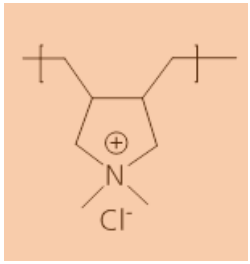
0.5% STABILIZER



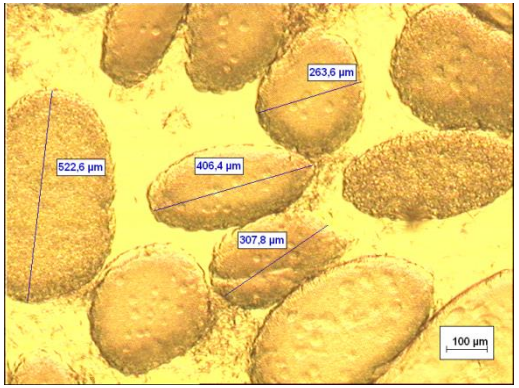
A: PEI M_n~25T G/MOL

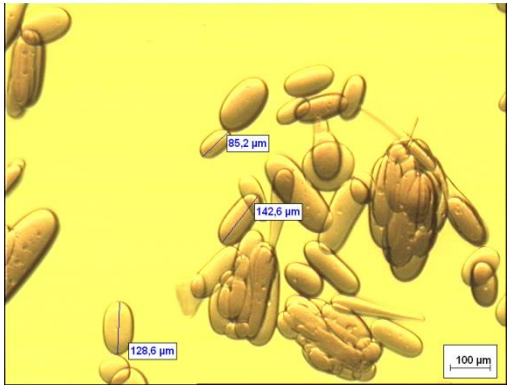


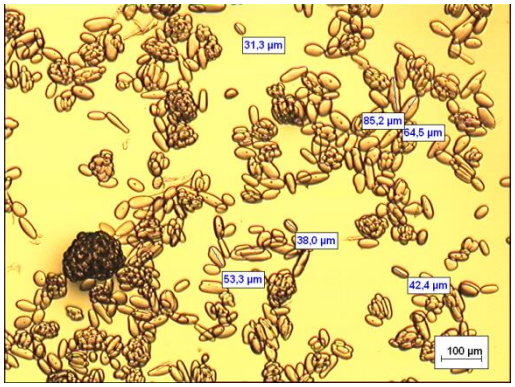
B: LUPAMIN 1595 M_n~10T G/MOL
DEGREE OF HYDROLYSIS 95%



C2: PQ 40U10 M_n~20T G/MOL







- VISCOSITY DURING SYNTHESIS OK, VERY FAST COALESCENCE AFTERWARDS IN ALL CASES
- BEST RESULT WITH POLY-DADMAC

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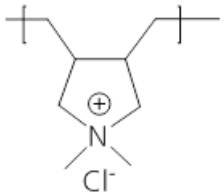
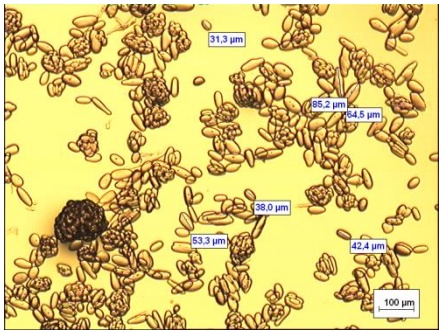
COMMERCIAL CATIONIC POLYMERS AS STABILIZERS

- VARIATION OF STABILIZER CONCENTRATION AND MOLECULAR WEIGHT

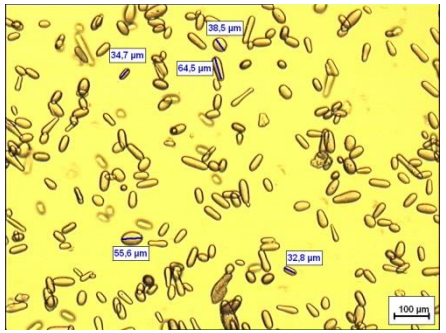


C2: PQ 40U10 M_n~20T G/MOL

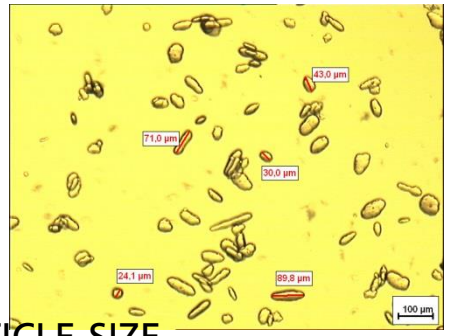
0.5% STABILIZER



1.0% STABILIZER



C1: PQ 40U05NV M_n~10T G/MOL



- HIGHER STABILIZER CONCENTRATION RESULTS IN LOWER PARTICLE SIZE
- LOWER MOLECULAR WEIGHT STABILIZER GIVES MORE OR LESS THE SAME RESULTS
- FAST COALESCENCE, PARTICLES WITH OVAL SHAPE → PRECIPITATION TOO „SOFT“

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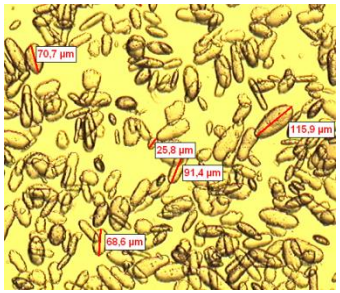
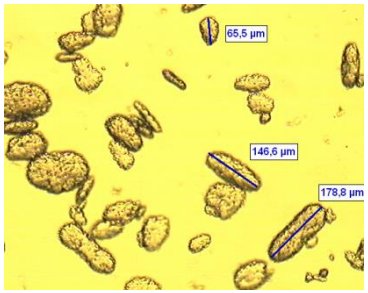
Variation of salt concentration

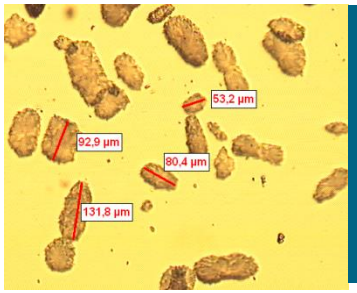
- Influence on precipitation:
  - High salt concentration → hard precipitation → low molecular weight since swelling of particles with monomers gets hindered
  - Low salt concentration → soft precipitation →high molecular weight but high viscosity of dispersion
  - Shape of particles is measure for type of precipitation
- Aim: small, spherical particles

VARIATION OF SALT CONCENTRATION

IN ALL CASES NO LONG TERM STABILITY, NO SPHERICAL PARTICLES

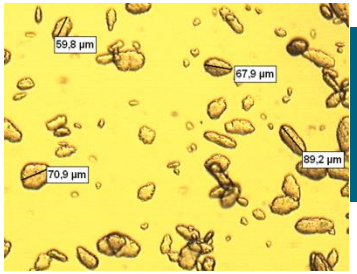






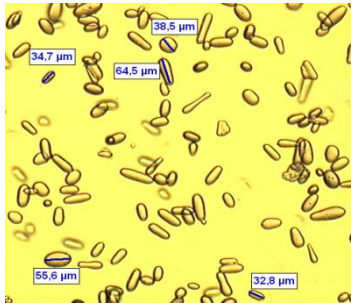
ALUM CONCENTRATION ↑
HARDER PRECIPITATION
LARGE ROUGH PARTICLES
(FORMED FROM MANY PRIMARY PARTICLES)

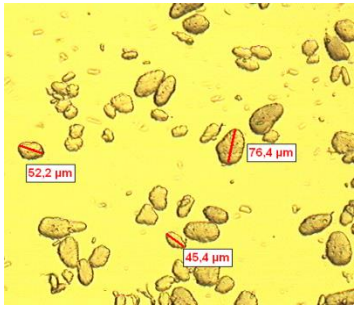
PAC CONCENTRATION ↓
ROUGH PARTICLES TRANSFORM BACK INTO SMOOTH OVAL ONES



PAC CONCENTRATION ↑
SAME TENDENCY AS INCREASE IN ALUM CONCENTRATION

STARTING POINT:
SOFT PRECIPITATION
SMOOTH OVAL PARTICLES





ALUM

PAC

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Design of stabilizer

- Hydrophilicity:

  stabilizer has to be soluble in continuous phase but increasing hydrophobicity within this limit leeds to lower viscosity of dispersion

- Molecular weight:

  too low → no long term stability due to missing steric stabilization

  too high → bridging of particles during polymerization

- Chain structure (statistic, block, graft)

  influences configuration of stabilizer at particle surface

- Type and density of charge for electrostatic stabilization

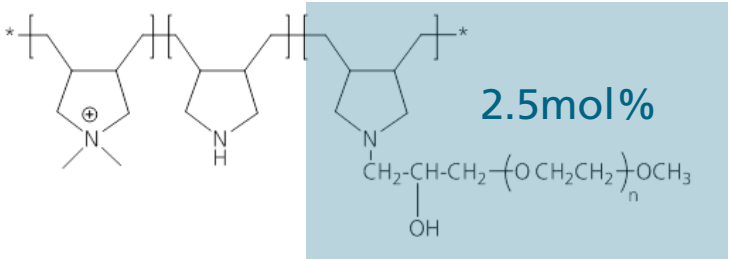
- Charged stabilizer acts as additional salt → fine-tuning of salt concentration

- After all mostly trial and error approaches

Design of stabilizer

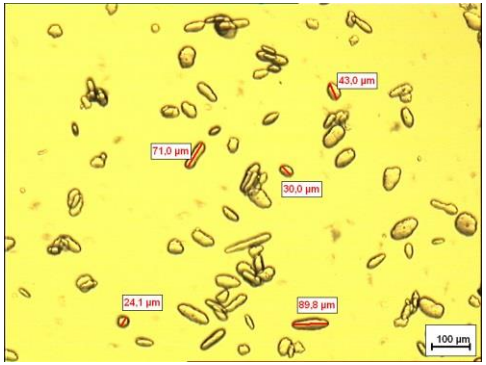
- Development based on PQ 40U05NV
  - Graft copolymers with PEG 350:

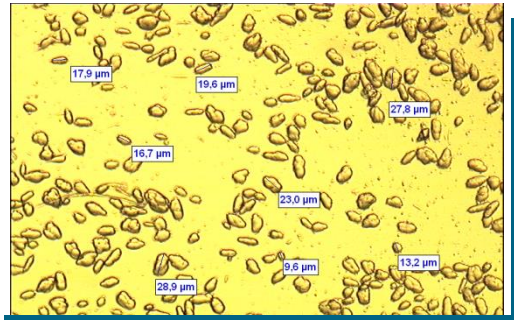
    Polyquat-g-PEG350



Amount of stabilizer

1.0%





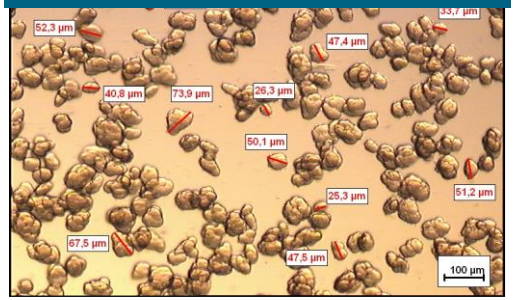
Tendency to spherical particles, still agglomeration
Stable for 3 weeks

By far smaller particles than with PEG-free polyquat

Optimization necessary

0.5%

Agglomeration of nearly spherical uniform particles



0

2.5

PEG in PQ mol%

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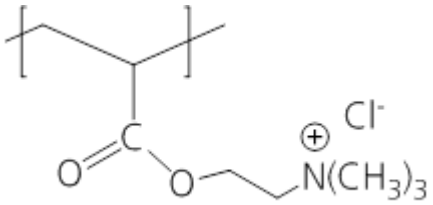
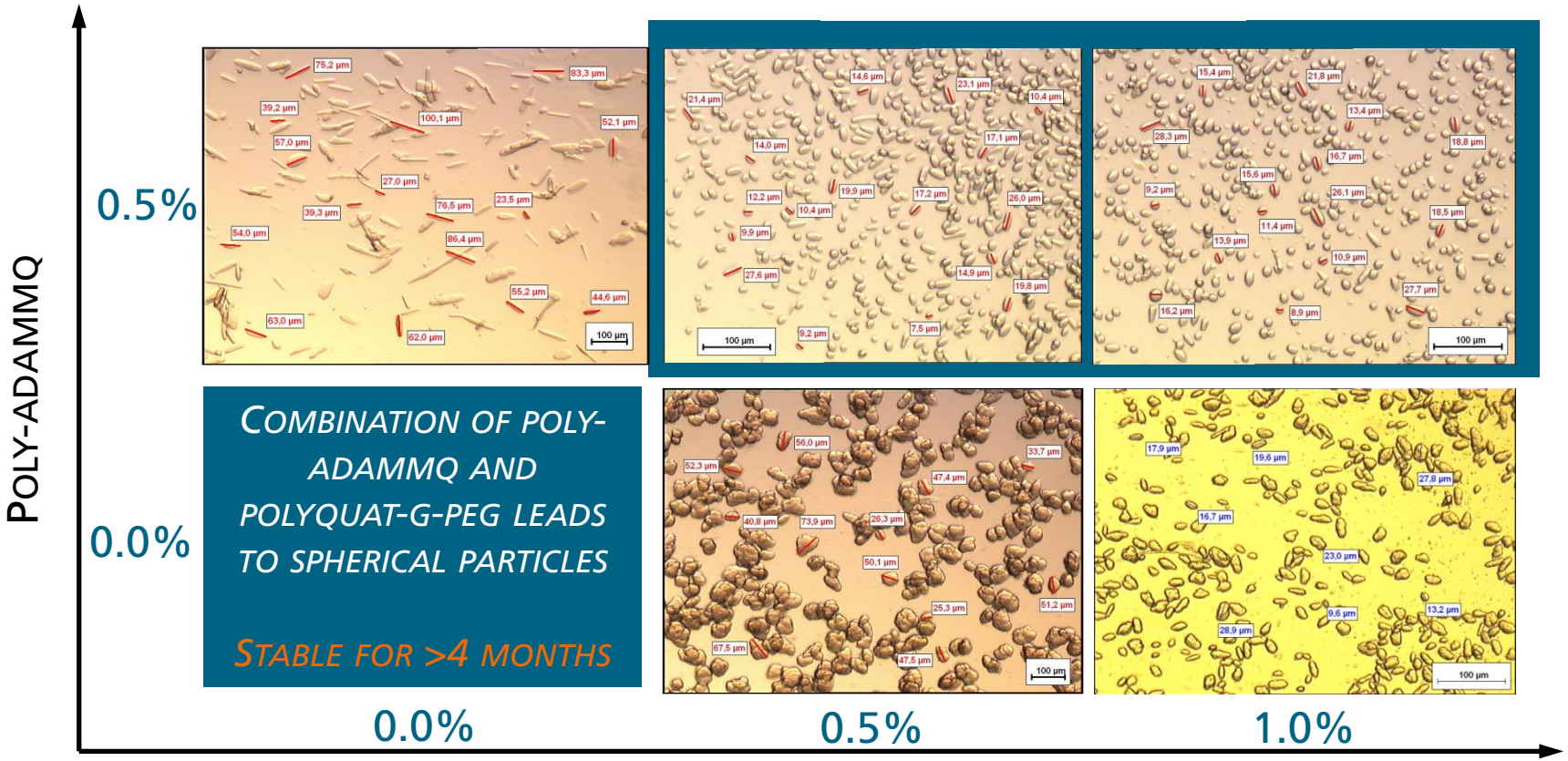
Final stabilizer

- Additional steric stabilization for long-term stability



POLY-ADAMMQ
M_n ~ 500T g/mol



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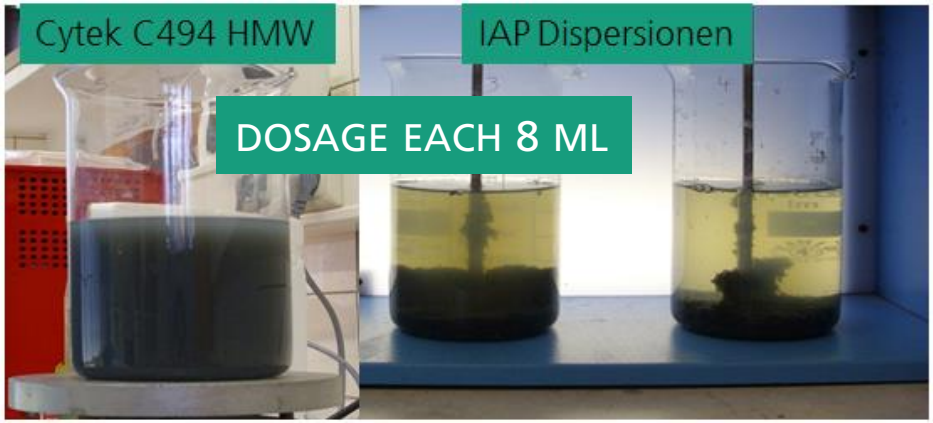
System limits

- *active* up to 25 wt%; increase of stabilizer concentration necessary
- *charge density* between 20% and 50% possible
  - Adjustment of salt and stabilizer concentration necessary
  - Commercial dispersions between 10 and 50%
  - Polymers with charge density <20% do not ptrecipitate in Al-salts
- molecular weights between 5 mio to 10 mio g/mol (MALLS)
  - Commercial benchmark 8 mio g/mol (MALLS)

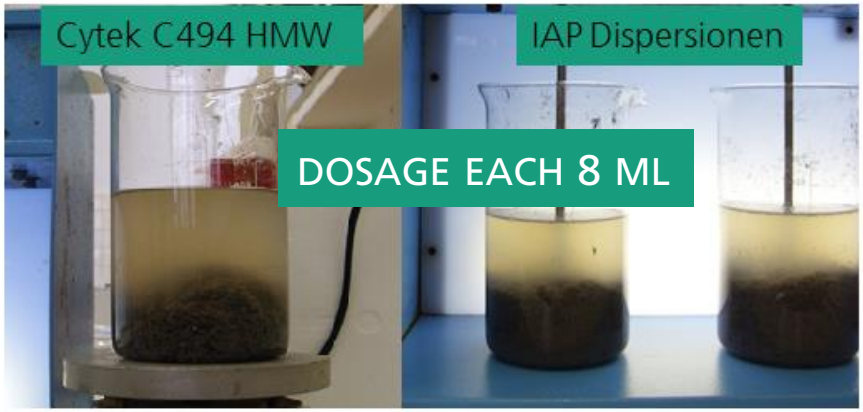
Application

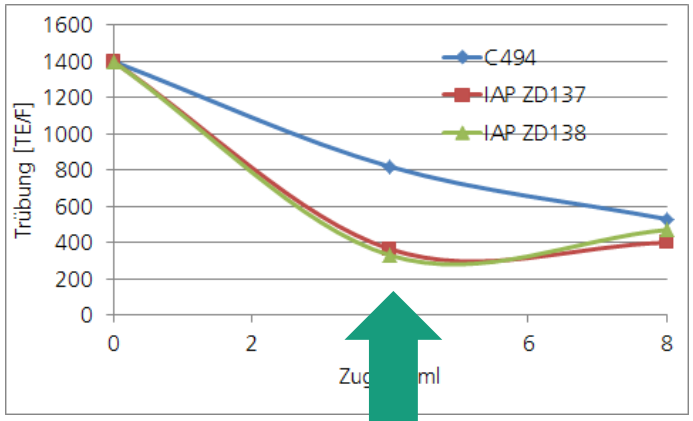
- *Application trials in „complicated“ waste waters at*
  - Lunzenauer Papier- und Pappenfabrik (circuit water)



BETTER FLOCCULATION AND LESS RESIDUAL TURBIDITY

  - Kübler & Niethammer (waste water from discoloration of used paper)





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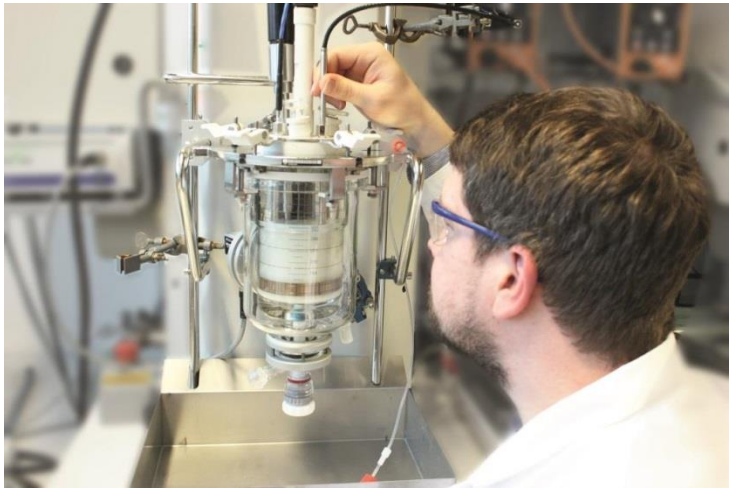
Summary

- Project was aimed on synthesis process for cationic polyelectrolytes using Al-salt solutions as continuous phase in a aqueous dispersion
- Suitable stabilizer system : combination of low molecular polyquat grafted with PEG and high molecular cationic polyelectrolyte
- Long-term stable dispersion with active contents up to 25% and charge densities between 20% and 50%
- Optimized initiator system and dosage gives conversions of 100% and molecular weights in the range of known aqueous dispersion systems
- Application trials point to advantages of the products in some complicated waste waters

New Opportunity for process development at FH-IAP

- Incorporation of **photon density wave sensor** into **RC1e** automated reaction calorimeter



- **Inline particle detection** for particles from 50nm to several mm (*PDW, FBRM and video microscopy*)

PDW ANALYTICS

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Thanks to

- The whole team:
  - Anita Schicktanz
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  - Dr. Mathias Hahn
  - Dr. Wolfram Palitzsch, Loser Chemie

- Arbeitsgemeinschaft industrieller Forschungsvereinigungen AiF

- ...and to you for your attention

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