Chemistry, synthesis, and characterization of functional polymers

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Present research topics in the laboratory

- Controlled Radical Polymerisation (ATRP, RAFT)
- Environmentally Responsive Polymers
- Globules and Mesoglobules in Aqueous Media
- Gold/Silver/Copper Nanoparticles
- Fluorinated Polymeric Surfactants
- Self-organization of Block Copolymers
- Computer Simulation of Polymer Systems with Complex Topology
- Characterization of Structures and Intermolecular Interactions of Polymers with Complex Architectures
- Polyelectrolyte Complexes
- Stimuli Responsive Hydrogels
- Nanocomposites
- New Cellulose/Polysaccharide Derivatives
- New Waterborne Coating Formulations

Semiflexible liquid crystals, simulation by Dr. Anna Zarembo
Examples of aqueous responsive polymers: poly(N-isopropylacrylamide) and poly(N-vinyl caprolactam)

Scheme 3. A model of the grafting of functional copolymers by PEO at two different temperatures in water: (a) before grafting; (b) after grafting; (c) at room temperature.

Virtanen, Janne: Self-Assembling of Thermally Responsive Block and Graft Copolymers in Aqueous Solutions
Doctoral dissertation, © University of Helsinki 2002

Laukkanen, Antti: Thermally responsive polymers based on N-vinylcaprolactam and an amphiphilic macromonomer,
Doctoral dissertation, © University of Helsinki 2005
Controlled radical polymerization

Case 1: ATRP (Satu Strandman, Anna Zarembo, Sami Hietala, Vladimir Aseyev)

- Synthesis of novel multifunctional initiators for star polymers
- Synthesis and characterisation of well-defined amphiphilic star block copolymers
- Self-assembling properties of the amphiphilic stars in aqueous solutions
Multifunctional ATRP initiators

Same number and structure of the initiating sites!

Type 1

Type 2 (with spacer)

1: $R = H$
2: $R = CH_3$
3: $R = H$
4: $R = CH_3$
Synthesis of the amphiphilic stars

\[
(\text{PMMA})_4 \\
(\text{PMMA}-b\text{-ptBA})_4 \\
(\text{PMMA}-b\text{-PAA})_4
\]
Saline solutions: CONTIN & Kratky representation on 4-armed stars

\[(\text{PMMA}_{73}-b-\text{PAA}_{143})_4\]

\[R_h = 62 \text{ nm and } 270 \text{ nm}\]

\[R_h(\text{mean}) = 111 \text{ nm}\]

\[R_g = \text{radius of gyration}\]
\[q = \text{amplitude of the scattering vector} = \frac{(4\pi n_0/\lambda_0)\sin(\theta/2)}{R_g}\]
\[P(q) = \text{particle scattering function} = \frac{R_0}{R_g}\]
cryoTEM and modeling of 4-arm stars

(PMMA$_{73}$-b-PAA$_{143}$)$_4$

no salt, pH 4.5

0.1 M NaCl, pH 4.5
Sticky star
(collaboration with Katja Jankova and Sören Hvilsted)

An image of a 42 g/L sample in water at 20° C.

Dynamic moduli of the polymer solutions in water at 20° C

Temperature dependence of the moduli of 26 mg/ml at 1 Hz oscillation frequency.
Case 2: RAFT
(Markus Nuopponen, Jun Shan, Katriina Kalliomäki et al.)

Thermoresponsive block copolymers, polymer protected gold nanoparticles, stereo block polymers
Conventional vs Controlled Radical Polymerization

- Short life-time – Rapid polymerization
- Uncontrolled side reactions
- Poor control over chain ends and molecular weights
- Broad molecular weight distribution

- Extended life-time of growing chains
- No irreversible chain transfer
- Narrow molecular mass distribution
- Accurate control over molecular mass and chain ends
RAFT
(Reversible Addition Fragmentation Chain Transfer)
Polymerization

$$P_n^* + P_m - X \xrightleftharpoons[k_{tr}]{k_{tr}} P_n - X + P_m^*$$

Cumyl dithiobenzoate

4-cyanopentanoic acid dithiobenzoate

S,S'-bis(a,a'-dimethyl-a''-acetic acid)-trithiocarbonate
RAFT polymerization

- Wide range of polymerizable monomers
- High molecular mass polymers
- Polymerizations in aqueous systems
Poly(N-isopropylacrylamide) - PNIPAM

- N-isopropylacrylamide

- Thermoresponsive polymer
- Soluble in water below 32 °C
- Phase separation above cloud point
Amphiphilic diblock copolymers with PNIPAM and hydrophobic blocks

Hydrophobic polystyrene

Hydrophilic PNIPAM

Size distributions of the aggregates at 20 °C.
a = PS48-PNIPAM346, b = PS75-PNIPAM118, c = P(t-BMA)135-PNIPAM123.

Cryo-electron microscopy images of aggregates
Tacticity

isotactic polymer

atactic polymer

Scheme 1. Free radical propagation in the presence and absence of a Lewis acid.\textsuperscript{[12]} LA: Lewis Acid.

A – B – A stereoblock polymers of NIPAM

A-B-A stereoblock polymers with atactic PNIPAM as a hydrophilic block (either A or B) and a non water-soluble block consisting of isotactic PNIPAM were synthesized using RAFT polymerizations.

a-i-a     i-a-i

atactic     isotactic
hydrophilic  water insoluble
A – B – A stereoblock polymers of PNIPAM

- When dispersed in water (low concentrations), the stereoblock polymers form, depending on the chain composition, branched micelle structures or spherical flower-like micelles.

- Stability and thermally induced collapse of micelles is strongly affected by block sequence.

Turbidity of aqueous solutions of PNIPAM polymers. \( i_2-a28-i2 \) (□), \( i_2-a40-i2 \) (○), \( a_{12}-i_{10}-a_{12} \) (■), \( a_{12}-i_5-a_{12} \) (●) and \( a_{24.3} \) (line) measured by UV-vis spectrometry (\( c = 1.0 \text{ g L}^{-1} \), heating rate = 0.2 °C min⁻¹).
Gold nanoparticles protected with RAFT polymers

- One-step synthesis of Au-PNIPAM-PMAA with a gold core, a PNIPAM inner shell and a PMAA corona.

\[
\text{PNIPAM-PMAA} + \text{LiB}(\text{C}_2\text{H}_5)_3\text{H} \xrightarrow{\text{THF/methanol}} \text{Au-PNIPAM-PMAA}
\]

- PMAA blocks control the colloidal stability of aggregates
- PNIPAM blocks showed an effect on the polarity of the immediate surrounding of the gold core
To conclude:

- Enormous progress in synthetic methods has taken place during the last ten years.

- Controll over molar mass and its distribution, even over the stereostructure is possible by simple radical polymerization reactions.

- Complex polymer structures.

- Fine tuning of polymer structures will lead to a multitude of new applications, e.g. to new smart carriers of active substances.