EXAM

1) ***Summary of the course, A4 both sides***
2) ***Explain briefly***
    a. ***Ligand (1p)***
    b. ***Maleimide-cysteine coupling in bioconjugation (1p)***
    c. ***Eczema tonsillitis (1p)***
    d. ***Bifurcated Dendron (1p)***
    e. ***Integrated first order kinetics rate law (2p)***
3) ***Living ATRP polymerization***
    a. ***Two graphs: $\ln(M_0/M)$ vs. t (linear lines of bulk and solution polymerization) and M_n vs conversion & dispersity vs. conversion – explain these and the linear relationship with the help of kinetic equations***
4) ***Step/condensation polymerization of nylon***
    a. ***Polymerization of adipic acid and hexamethylene diamine. Draw the chemical reaction. What type of reaction is it? (Step polymerization)***
    b. ***What is the Mn if C = 99,5%? ($Mn = X * M_0$, $M_0 = M_{1,0} + M_{2,0} - M_{H_2O}$, ~ 45 000 g/mol)***
    c. ***Benzoic acid (one -COOH group!) is added. What is the ratio of** adipic acid : hexamethylene diamine : benzoic acid **needed to reach M_n of 10 000 g/mol?***

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Step polymerization

Condensation polymers

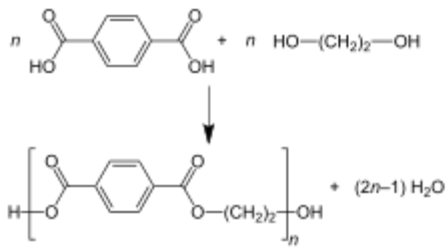
- Two different monomers react together and some small molecule is eliminated (e.g. water, alcohol)
- Polycondensation
  - C = conversion (%) = $((N_0 - N/N_0) * 100\% = p$
  - P = degree of polymerization = $1/(1-p)$
- Rate law: $v = k[A]^a[B]^b$
  - k = rate constant
  - a + b = overall reaction order (in this course only 1st and 2nd)
- 1st order reactions:

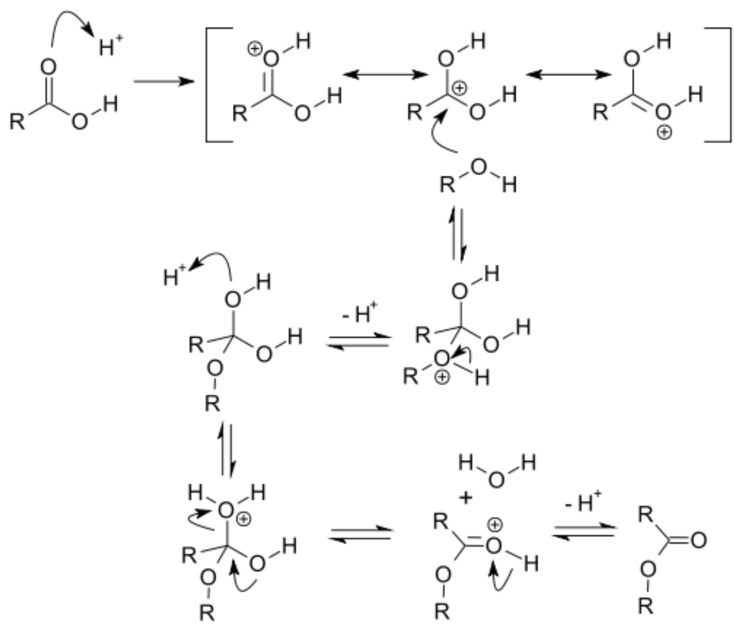
$$\frac{d[A]}{dT} = -k[A] \quad \text{the integrated form is} \quad \ln\left(\frac{[A]}{[A]_0}\right) = -kt \rightarrow [A] = [A]_0 e^{-kt}$$

- 2nd order reactions:

$$\frac{d[A]}{dT} = -k[A]^2 \quad \text{the integrated form is} \quad \frac{1}{[A]} - \frac{1}{[A]_0} = kt \rightarrow [A] = \frac{[A]_0}{1 + kt[A]_0}$$

- Polyesters
  - PET: ethylene glycol (or polyethylene-oxide) + terephtalatic acid + H^+ (catalytic amount)
    - Electrodeficient (electrophile) carboxyl group reacts with hydroxyl group (nucleophile)
    - Tautomerism: reorganization of a molecule





Esterification

  - Polyesterification mechanism: COOH-groups gradually disappear which can be used to determine the state of polymerization
- Polyamides
- Polyurethanes
- Reaction occurs in lower temperature with more effectively cleaving groups (e.g. HCl > H_2O)

- Molecular weight control in linear polymerization
  - Usually a very specific MW is wanted
  - DOP depends on polymerization time

Chain polymerization

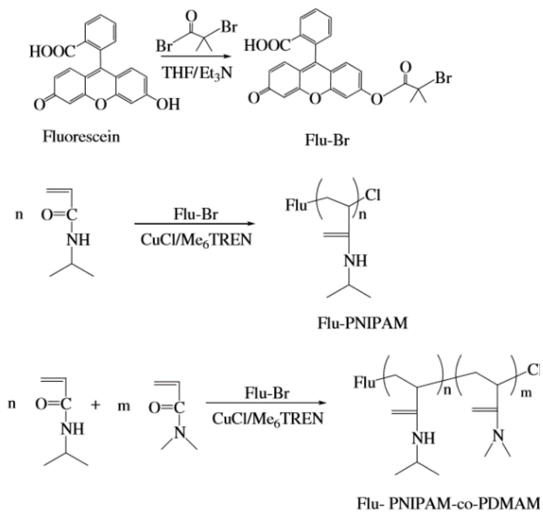
- An activated monomer M attacks another monomer, links to it, then that unit attacks another monomer etc.
- Monomer is used up slowly
- High-molecular-weight polymers are formed rapidly and only the yield, not the average molar mass of the polymer increases with longer reaction time
- Monomers usually include double bonds
- Reactive species can be radical, cationic or anionic

Chain transfer

- Premature termination usually causes the observed molecular weight to be smaller than predicted

POSTERWORK

- What was made?k
  - *N*-isopropylacrylamide-*N, N*-dimethylacrylamide-copolymer (Flu-NIPAM-co-DMAM)
  - Thermo-sensitive fluorescent copolymers with critical solution temperature close to body temperature
  - Applications: biosensors, enzyme recovery, triggered drug release, affinity separations
- How was the polymerization carried out?
  - A fluorescent initiator, fluorescein 2-bromoisobutyrate (Flu-Br) was synthesized
  - ATRP with Flu-Br, Me_6TREN as ligand and CuCl as catalyst -> poly(*N*-isopropylacrylamide) (NIPAM)
    - 0,1 mmol Flu-Br; 0,1 mmol CuCl; 0,1 mmol ligand; 0,02 mol NIPAM
  - Monomer feed changed to *N, N*-dimethylacrylamide (still ATRP with Flu-Br) -> Flu-NIPAM-co-DMAM
    - 0,1 mmol Flu-Br; 0,1 mmol CuCl; 0,1 mmol ligand; 9 mmol NIPAM; 1 mmol DMAM



- Kinetics of the polymerization
  - First order kinetics, plot of $\ln([M]_0/[M])$ showed a nonlinear curvature after three hours
    - Decreasing polymerization rate over time
  - Linear increase of M_n with conversion
- Polymer purification
  - Passage of the solution over a basic alumina column (NIPAM)
  - Isolation by precipitation in cold diethyl ether and vacuum drying (NIPAM)
- Polymer characterization
  - M_W and PDI (dispersity) by GPC (samples taken periodically during polymerization)
  - Conversion by gravimetry (samples taken periodically during polymerization)
  - LCST (lower critical solution temperature) by cloud points measurements
  - Fluorescence spectroscopy
  - ^{1}H NMR spectrometry for more precise M_W