

Seminar zur Vorlesung
„Polymermaterialien“

Übung 3
Ringöffnungspolymerisation

SS 2019

21.05.2019, Dienstag, 7:30 Uhr

Raum: 1/232

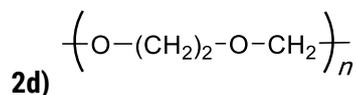
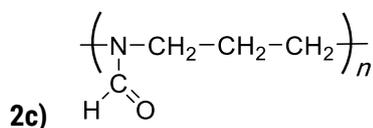
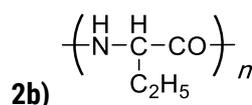
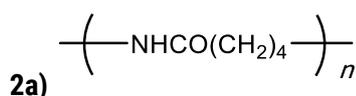
Literaturempfehlung: George Odian: *Principles of Polymerization*, 4. Auflage, Kapitel 7, ISBN 0-471-27400-3

1) Consider the following monomers and initiating systems:

Initiating System	Monomer
$n\text{-C}_4\text{H}_9\text{Li}$ $\text{BF}_3 + \text{H}_2\text{O}$ H_2SO_4 NaOC_2H_5 H_2O	Propylene oxide α -Pyrrolidone Ethylenimine Octamethylcyclotetrasiloxane Propylene sulphide Trioxane

Which initiating system(s) can be used to polymerize each of the various monomers?
Show the mechanism of each polymerization by chemical equations.

2) Give the cyclic monomer(s), initiator, and reaction conditions necessary to synthesize each of the following polymers:



3) Discuss the effect of ring size on the tendency of a cyclic monomer toward ring-opening polymerization!

- 4) The polymerization of an epoxide by hydroxide or alkoxide ion is often carried out in the presence of an alcohol. Why? How is the degree of polymerization affected by alcohol? Discuss how the presence of alcohol affects both the polymerization rate and molecular weight distribution.
- 5) Explain the following observations:
- 5a.** A small amount of epichlorohydrin greatly increases the rate of the polymerization of tetrahydrofuran by BF_3 even though epichlorohydrin is much less basic than tetrahydrofuran.
- 5b.** The addition of small amounts of water to the polymerization of oxetane by BF_3 increases the polymerization rate but decreases the degree of polymerization.
- 6) T. Saegusa, H. Fujii, S. Kobayashi, H. Ando, and R. Kawase, *Macromolecules*, 6, 26 (1973), have found that the polymerization rate for the BF_3 polymerization of oxetane follows this Equation:

$$-\frac{d[M]}{dt} = k_p[P^*][M]$$

- 6a.** Describe by an equation the mechanism for the propagation step in this polymerization.
- 6b.** The values of k_p at -20°C are 0.18 and $0.019 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively, for polymerizations carried out in methylcyclohexane and methylene chloride. Explain why propagation is faster in the less polar solvent.
- 6c.** The following rate constants and activation parameters for propagation were observed for oxetane and 3-methyloxetane in CH_2Cl_2 :

	Oxetane	3-Methyloxetane
k_p at -20°C ($\text{L} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$)	0.019	0.11
ΔG^\ddagger_p (kJ/mol)	71.2	65.7
ΔH^\ddagger_p (kJ/mol)	57.4	65.3
ΔS^\ddagger_p ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	-50.7	-5.4

Discuss why 3-methyloxetane is more reactive than oxetane. Is a negative entropy of activation for propagation consistent with the proposed propagation mechanism?