Microwave-assisted Polymer Synthesis: A New Technology at its Outset

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Outline

Introduction
Polymerizations under microwave heating (MWH)

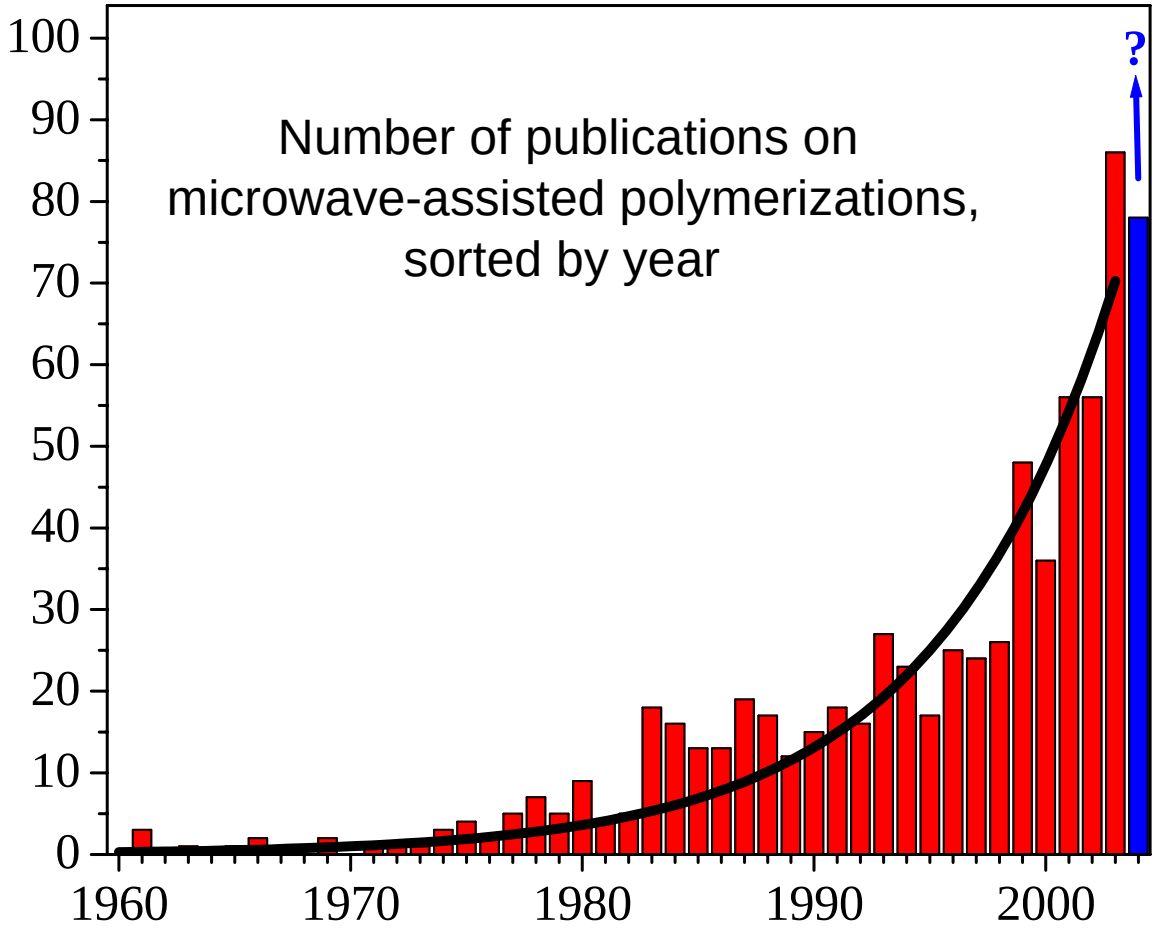
Polymerization of 2-ethyl-2-oxazoline
Livingness / First-order kinetics / Bulk polymerization / High molecular weights

Polymerization of other 2-oxazolines
Livingness / First-order kinetics / Bulk polymerization / High molecular weights

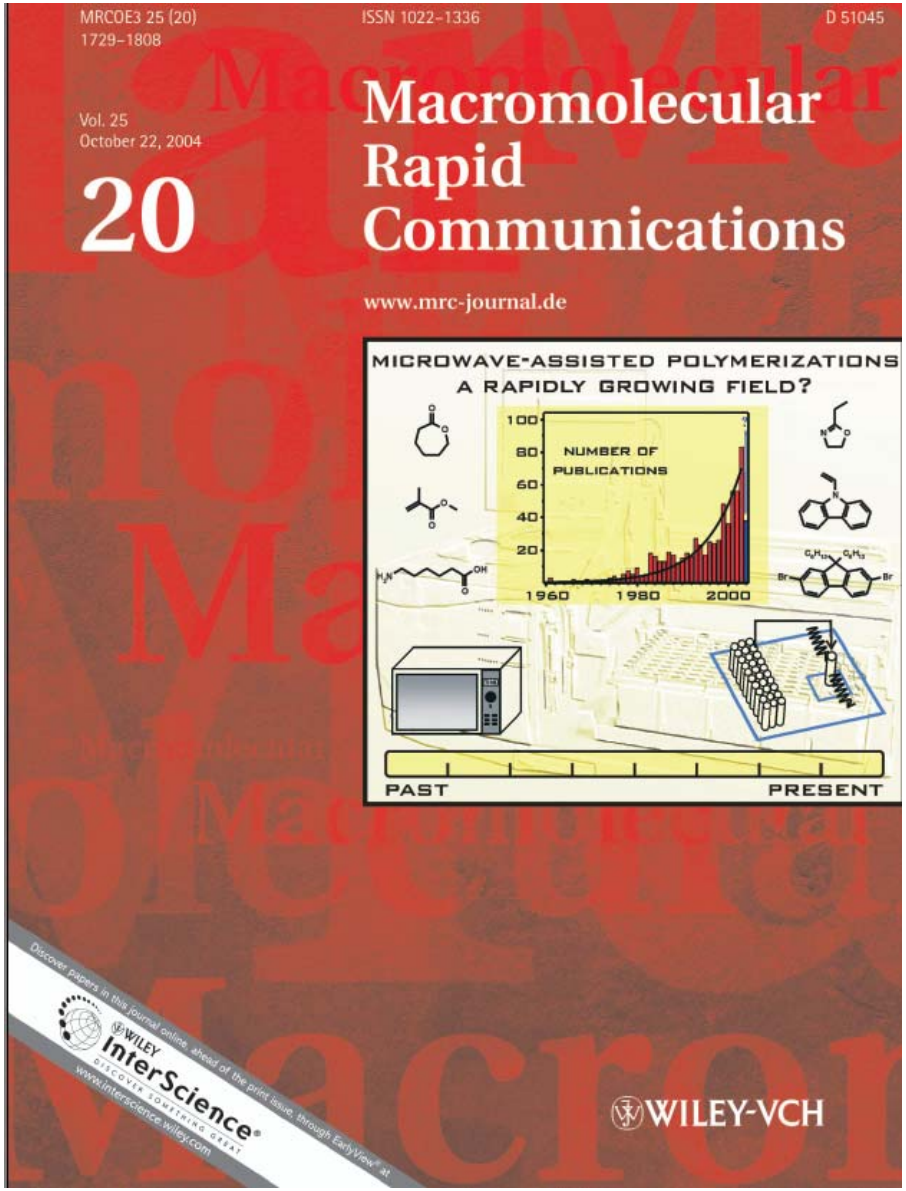
Diblock copoly(2-oxazolines)
Motivation / Library synthesis / Characterization by GPC and NMR / Surface energy

Conclusions and Outlook

Polymerizations under MWH

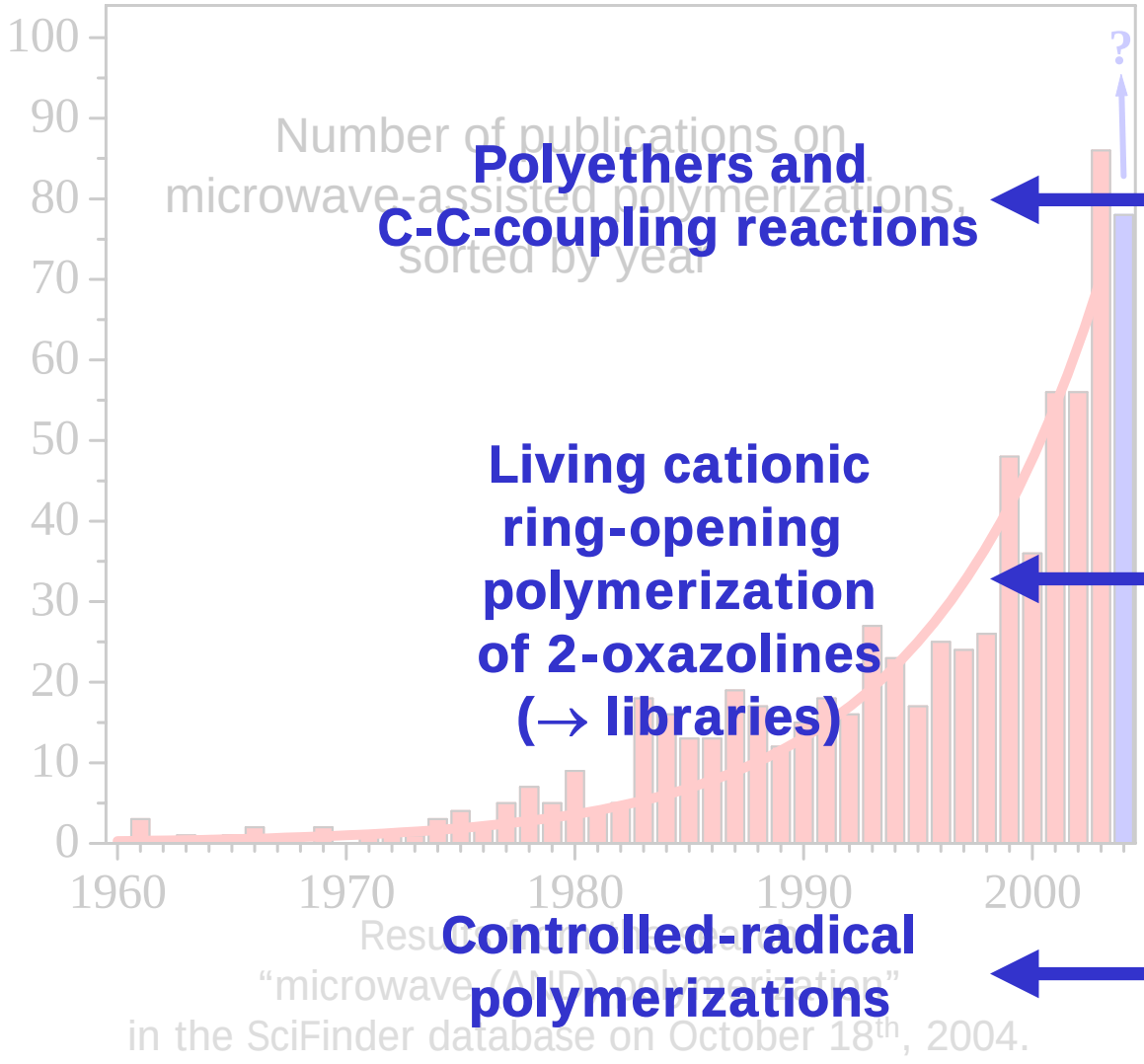


Results from the search
"microwave (AND) polymerization"
in the SciFinder database on October 18th, 2004.



F. Wiesbrock, R. Hoogenboom, U. S. Schubert, *Macromol. Rapid Comm.* **2004**, *25*, 1739-1764.

Polymerizations under MWH



Polyethers and C-C-coupling reactions

Living cationic ring-opening polymerization of 2-oxazolines (→ libraries)

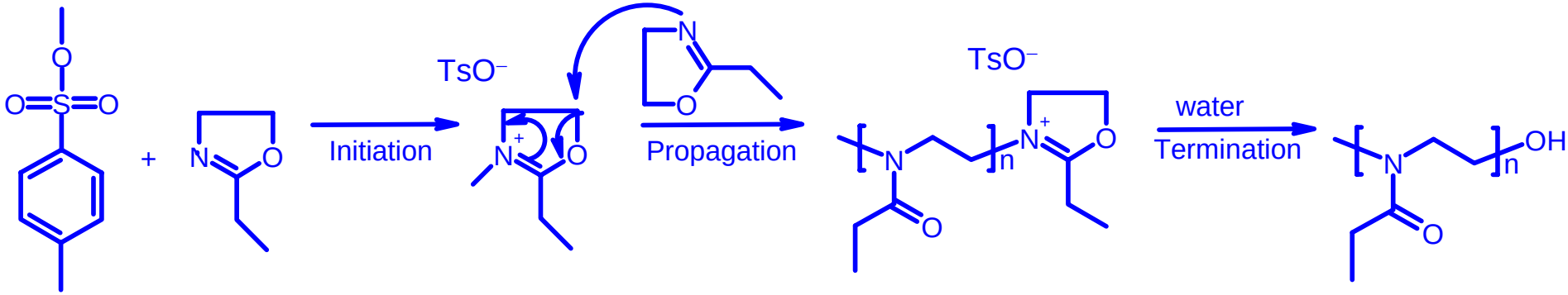
Controlled-radical polymerizations

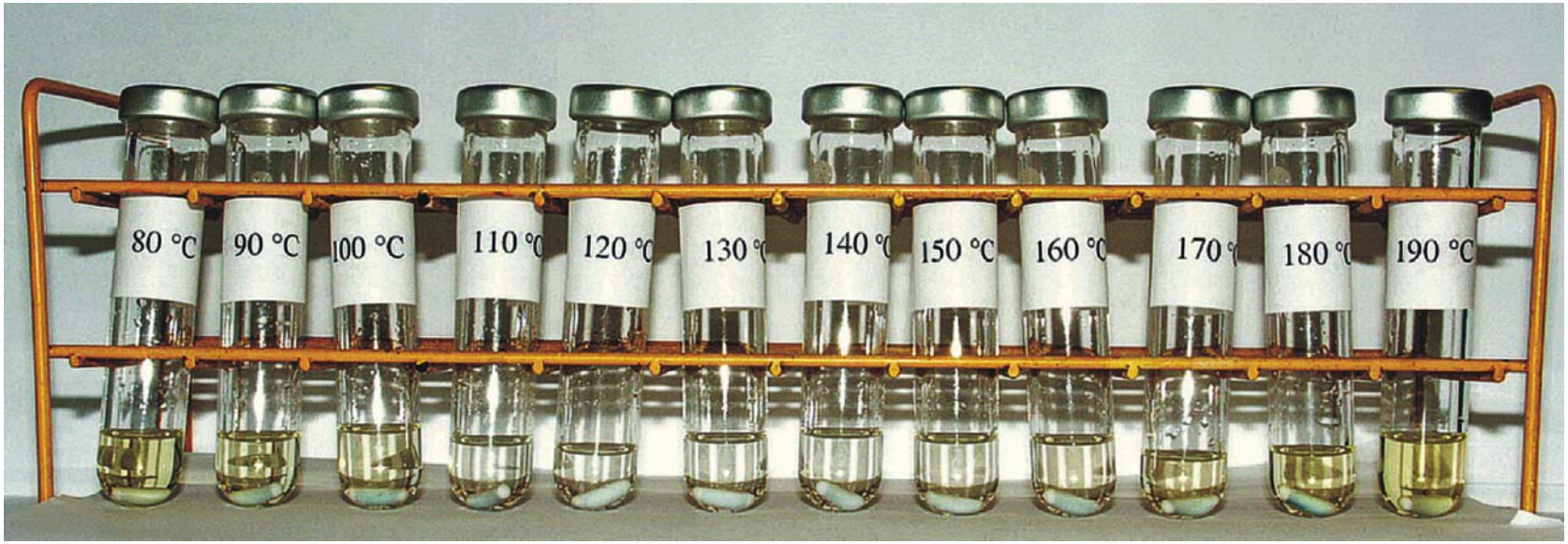
Step-growth polymerization reactions carried out for polyamides and polyimides

Ring-opening polymerization reactions performed (almost) exclusively on caprolactones and -lactames

Radical polymerizations: Focus on MMA and styrene

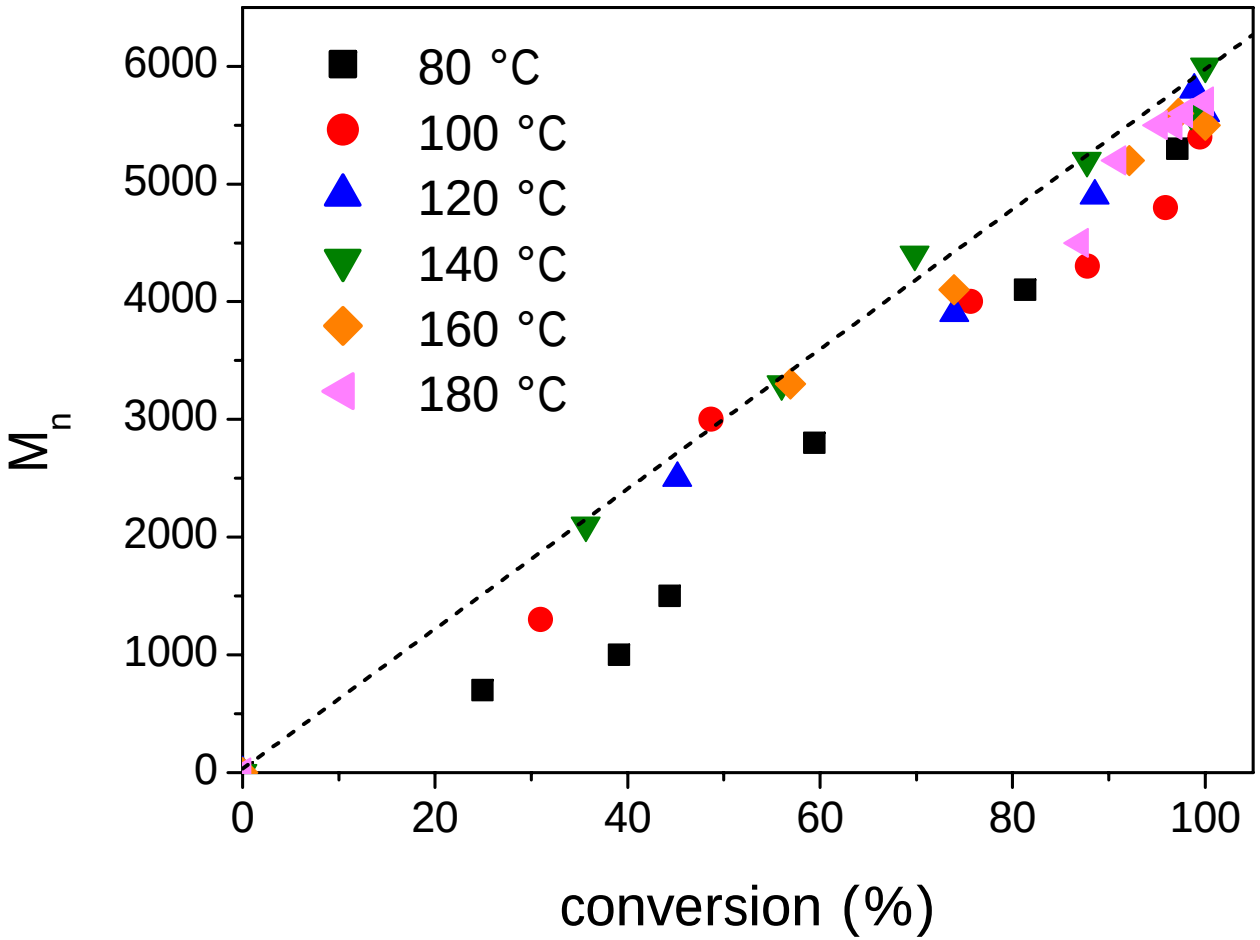
Polymerization of 2-ethyl-2-oxazoline





F. Wiesbrock, R. Hoogenboom, C. H. Abeln, U.S. Schubert, *Macromol. Rapid Comm.* **2004**, *25*, 1895-1899.

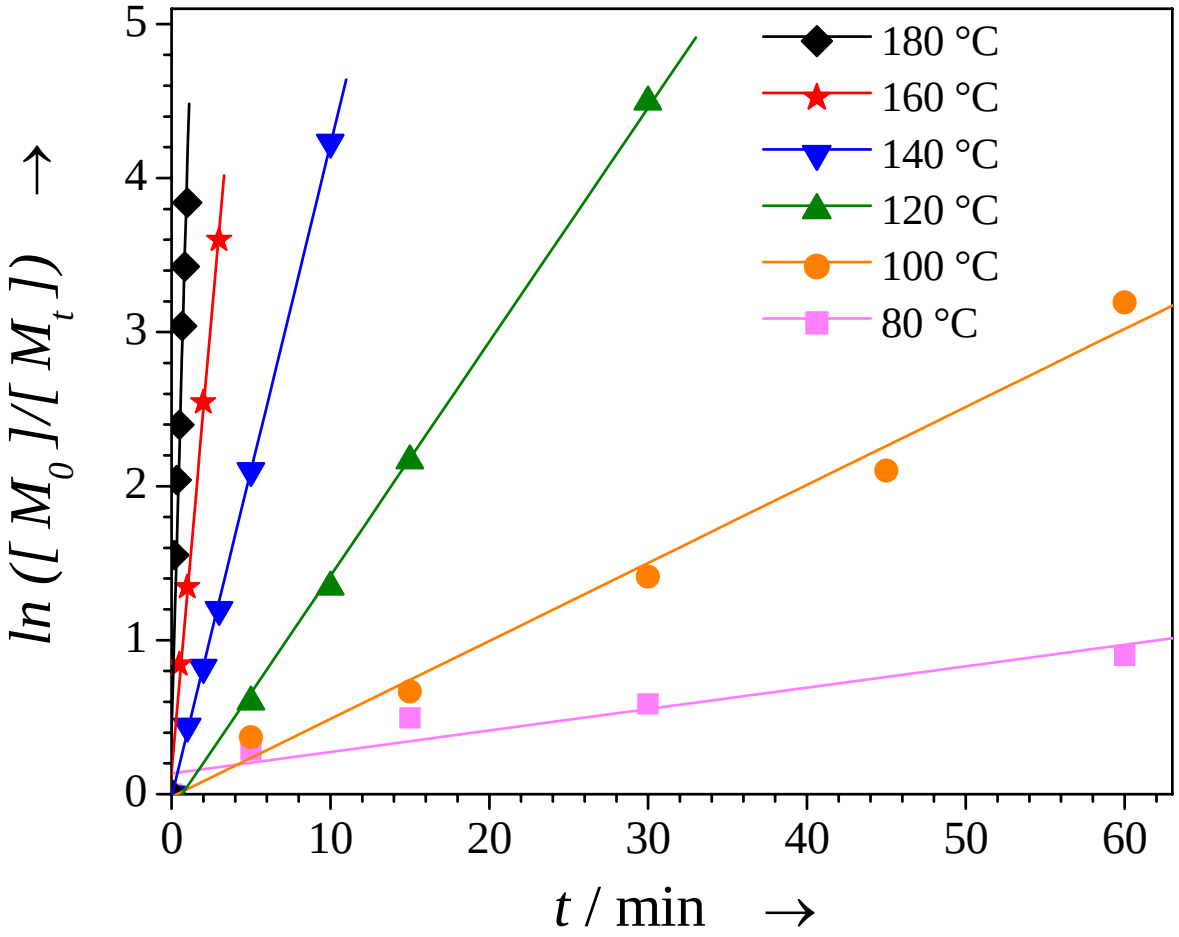
Poly(2-ethyl-2-oxazoline): Livingness



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

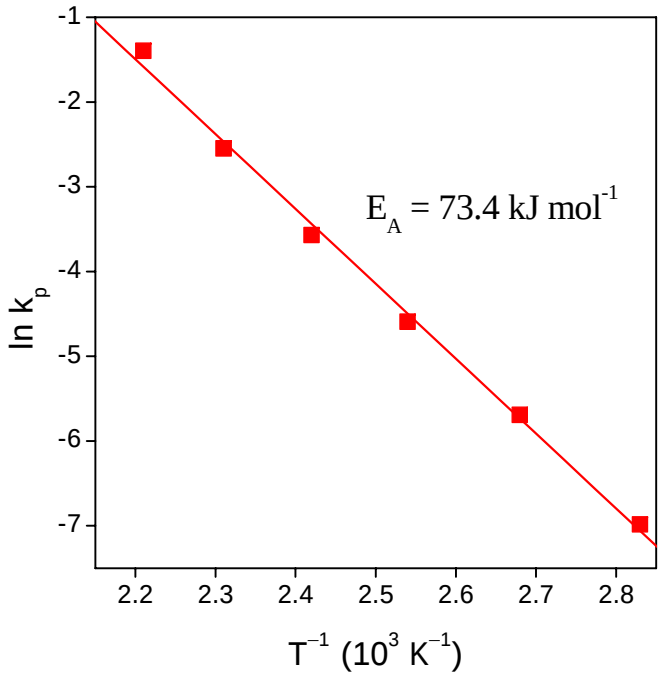
$$\Rightarrow \ln \frac{[M_0]}{[M_t]} = k_p \cdot [I_0] \cdot t$$

Poly(2-ethyl-2-oxazoline): Kinetics

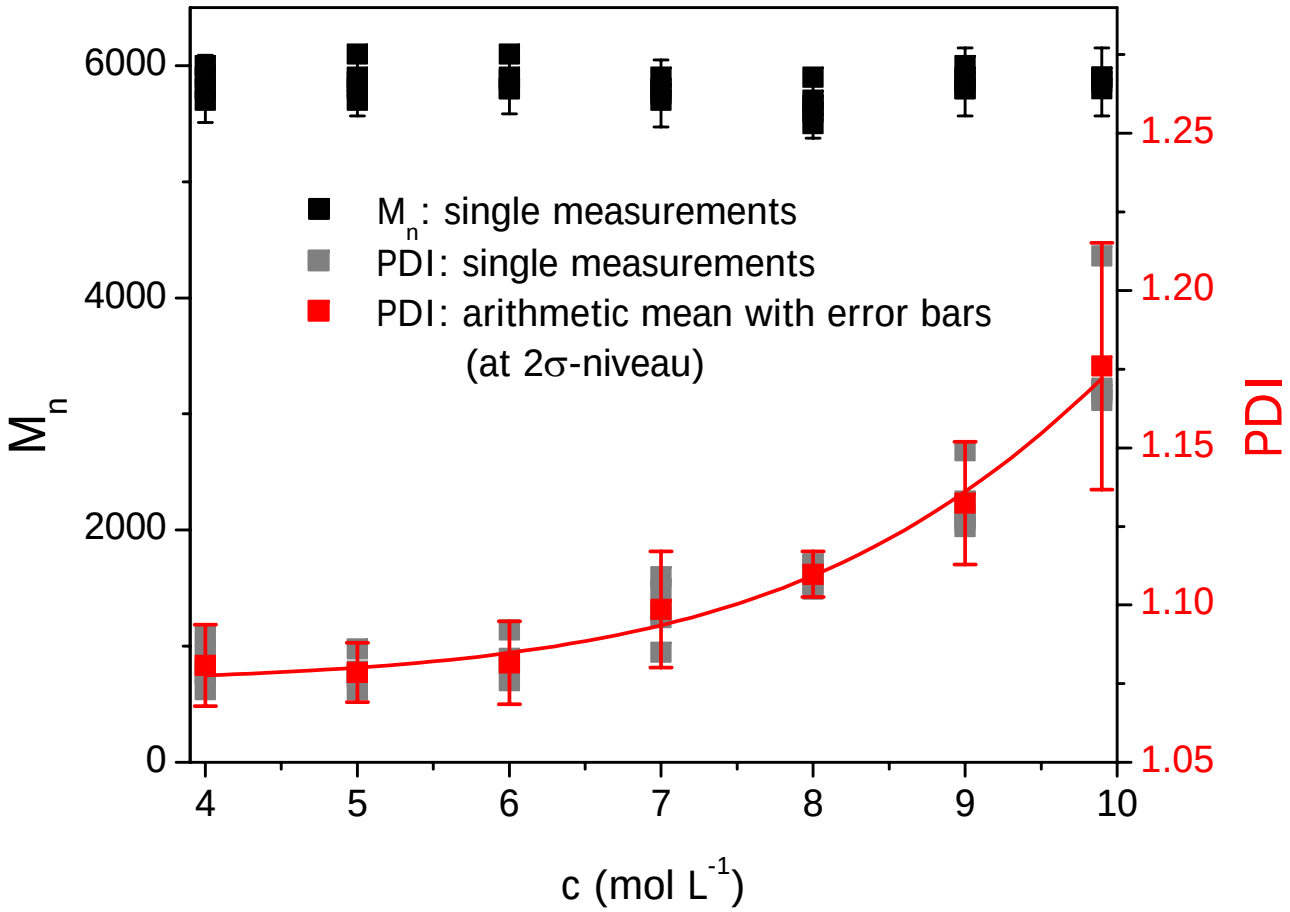


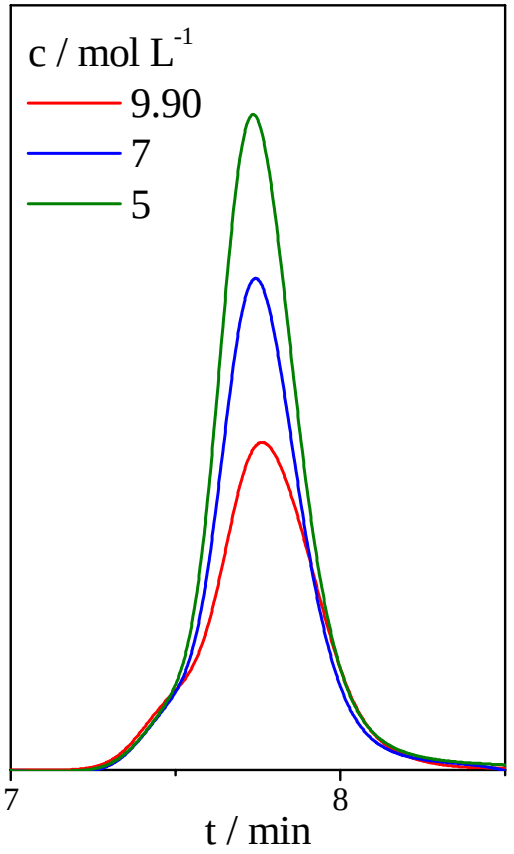
$$k_p = A \cdot e^{-\frac{E_A}{RT}}$$

$$\Rightarrow \ln k_p = \ln A - \frac{E_A}{R} \cdot \frac{1}{T}$$

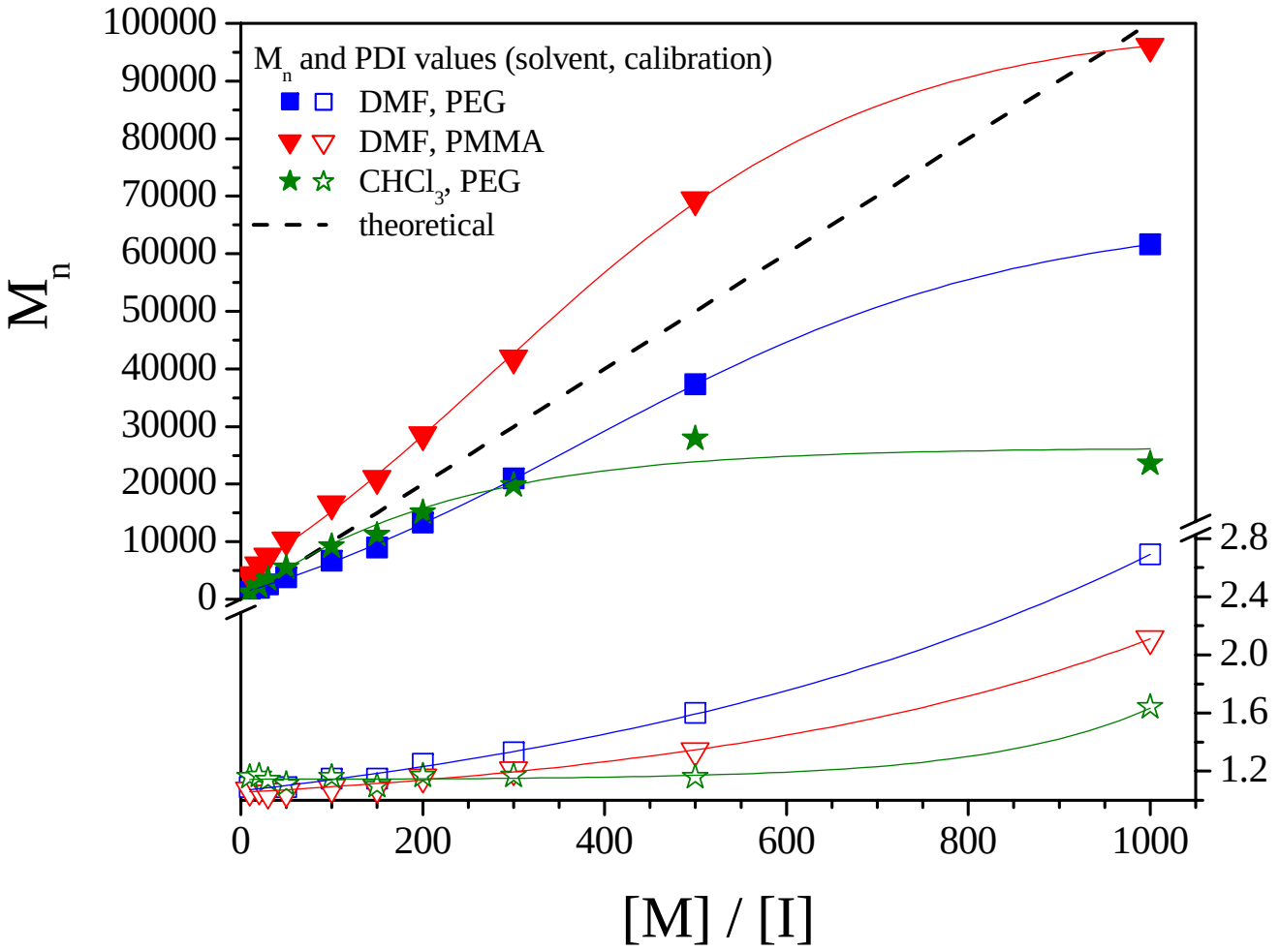


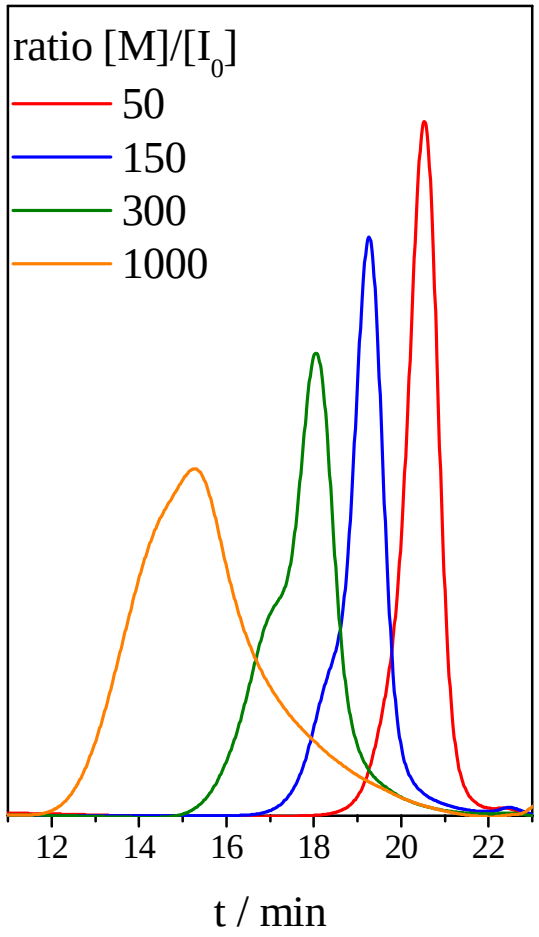
Poly(2-ethyl-2-oxazoline): Bulk polym.





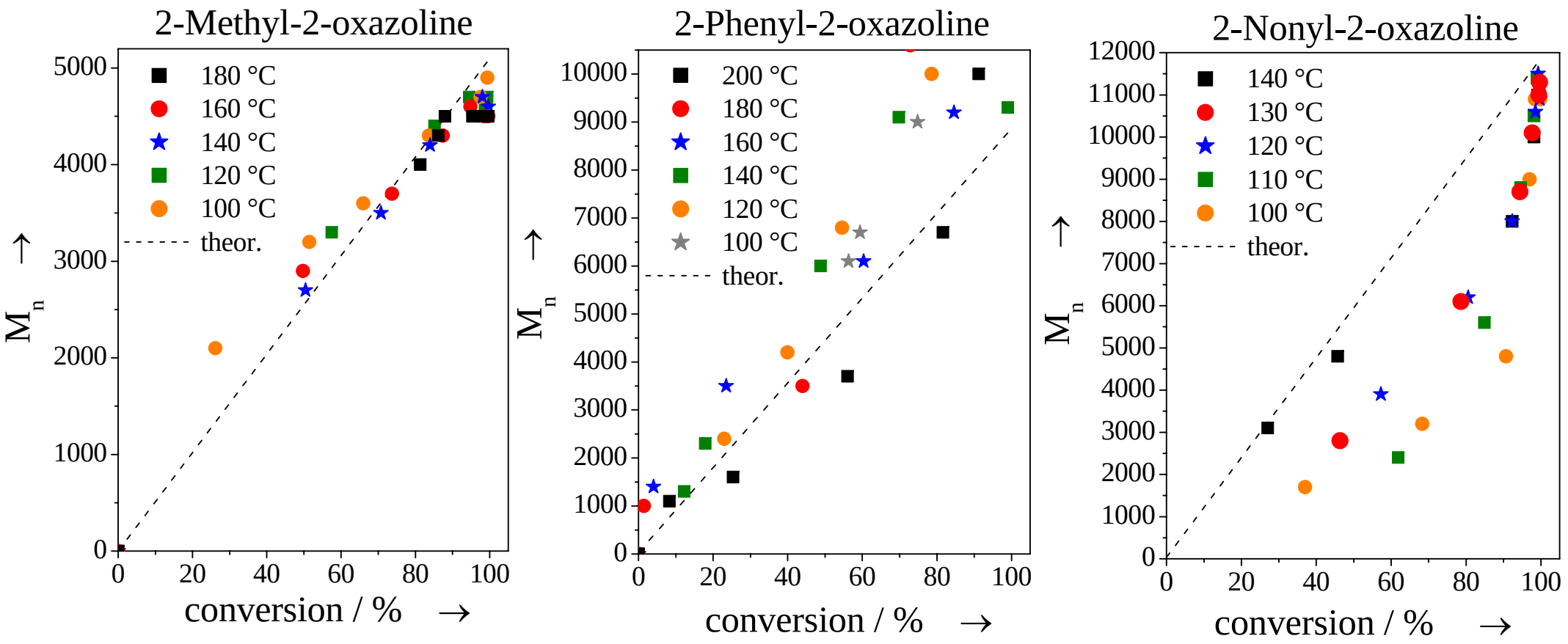
Poly(2-ethyl-2-oxazoline): Higher M_n





Other 2-oxazolines: Livingness

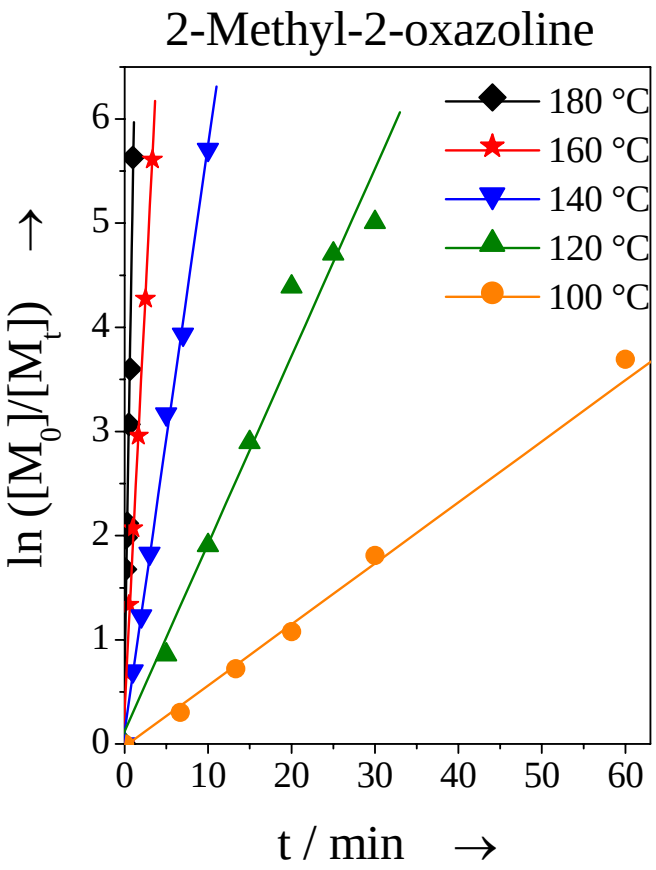
The number average molecular weights depend linearly on the monomer conversion.

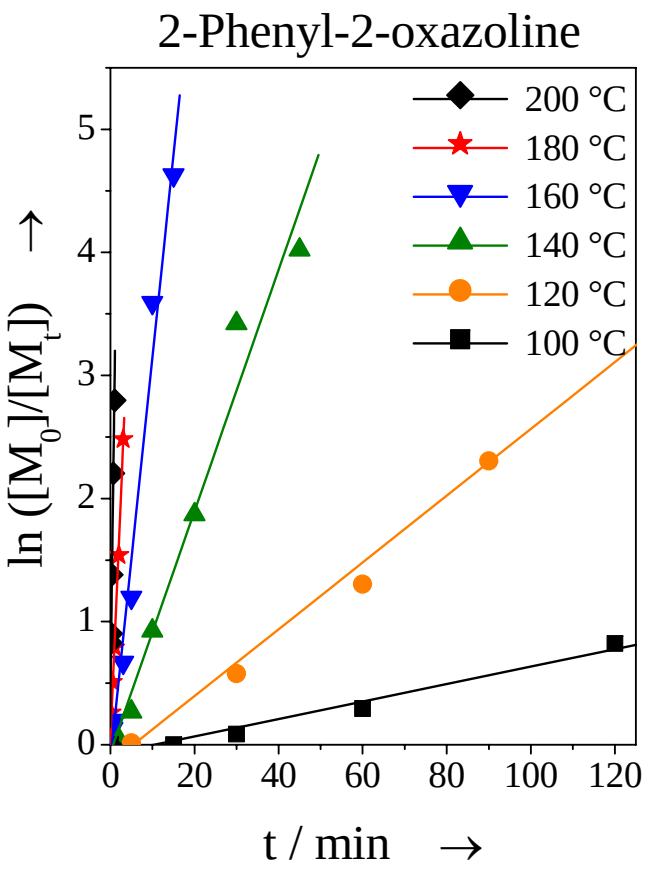


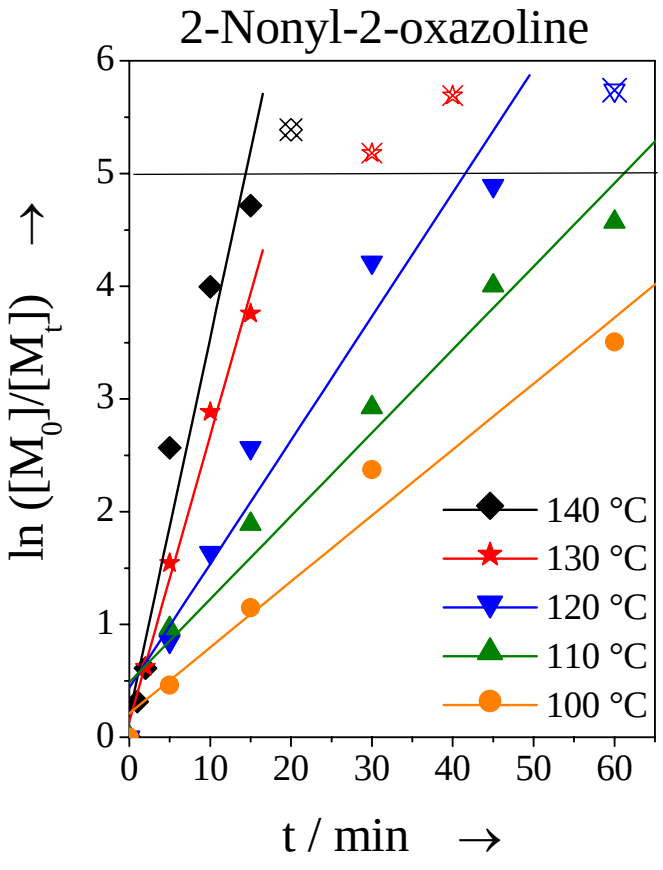
R. Hoogenboom, F. Wiesbrock, M. Leenen, M.A.R. Meier, U.S. Schubert, *submitted*.

Other 2-oxazolines: First-order kinetics

Kinetic analysis

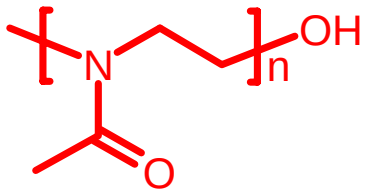




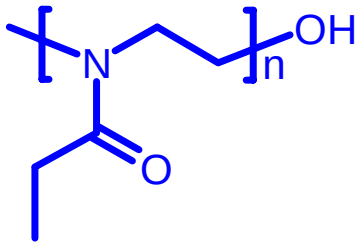


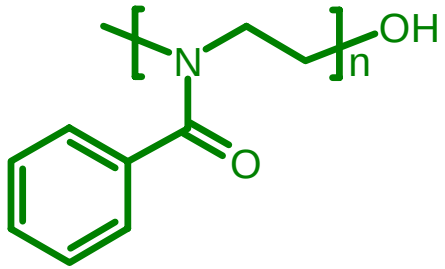
F. Wiesbrock, R. Hoogenboom, M. Leenen, U.S. Schubert, *submitted*.

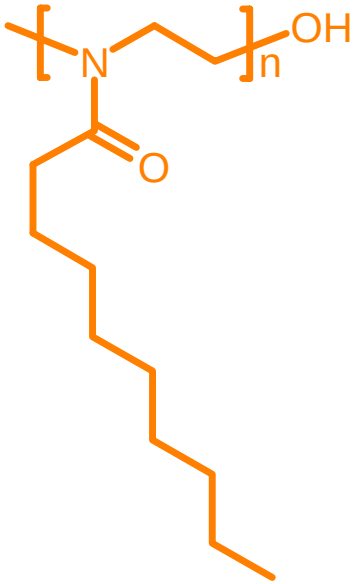
Polymerization of 2-oxazolines

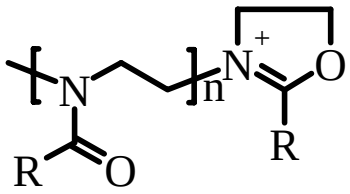


Monomer	Frequency factor A 10^{11} L mol^{-1} s^{-1}	Activation energy E_A kJ mol^{-1}
2-Methyl-2-oxazoline	18.0	75.4
2-Ethyl-2-oxazoline	7.17	73.4
2-Phenyl-2-oxazoline	53.8	84.4
2-Nonyl-2-oxazoline	4030.2	78.5



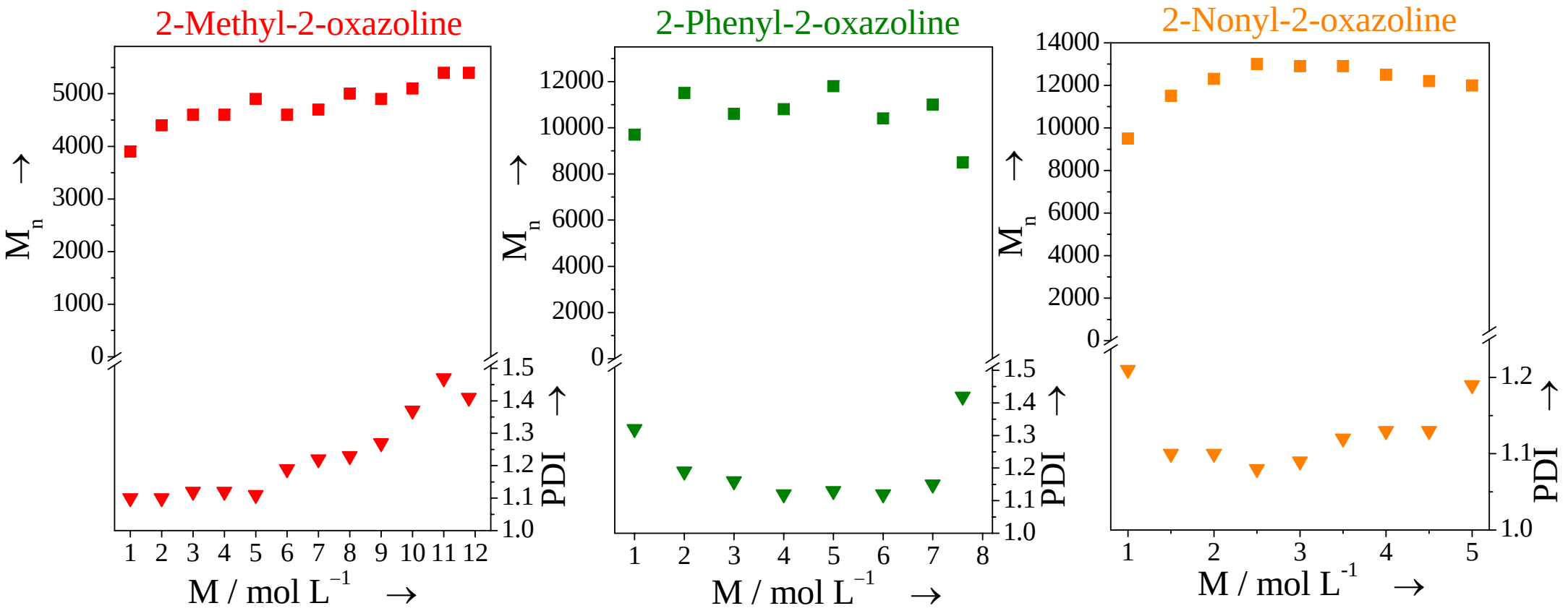






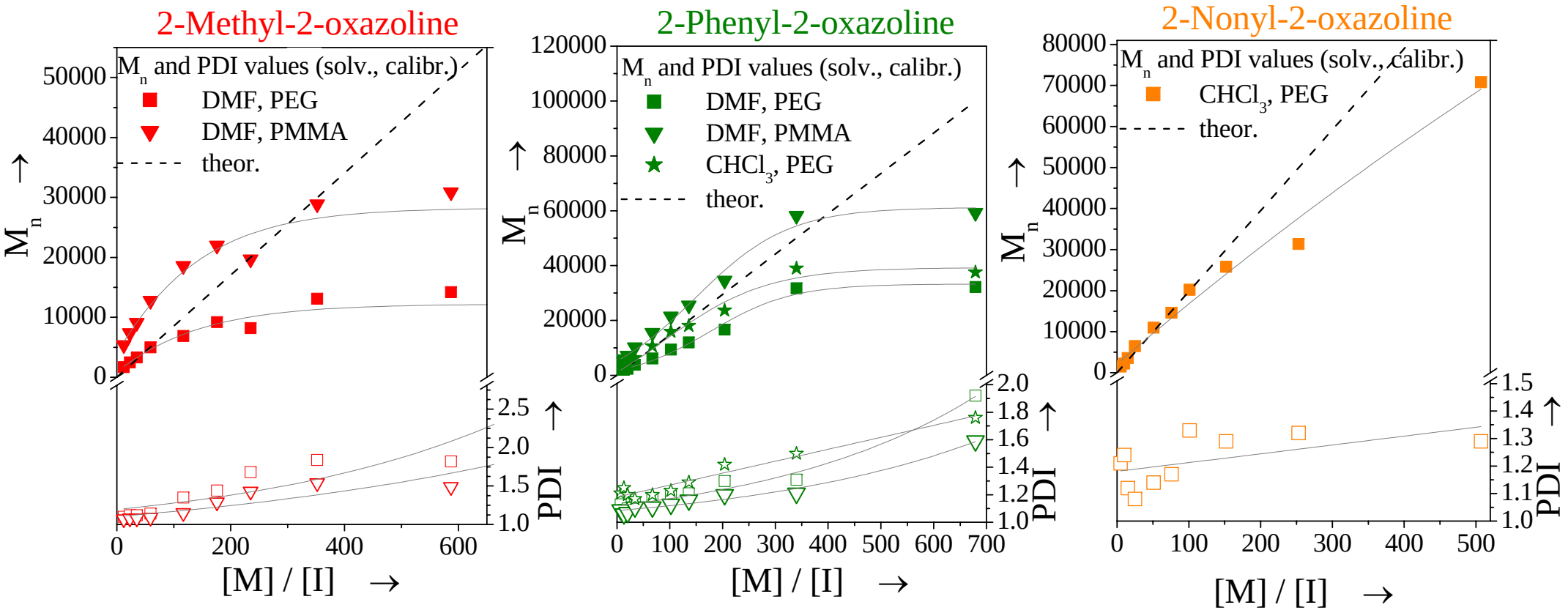
2-oxazolines: Bulk polymerization

Reduced solvent amounts



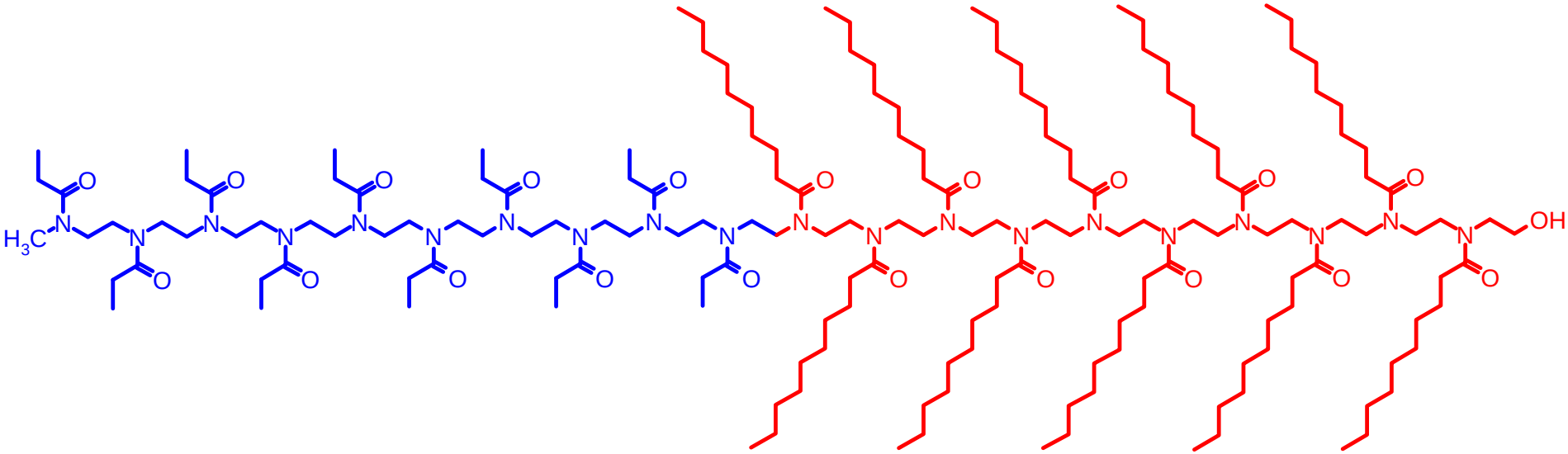
2-oxazolines: Higher M_n

High molecular weight polymers



Diblock copoly(2-oxazoline)s

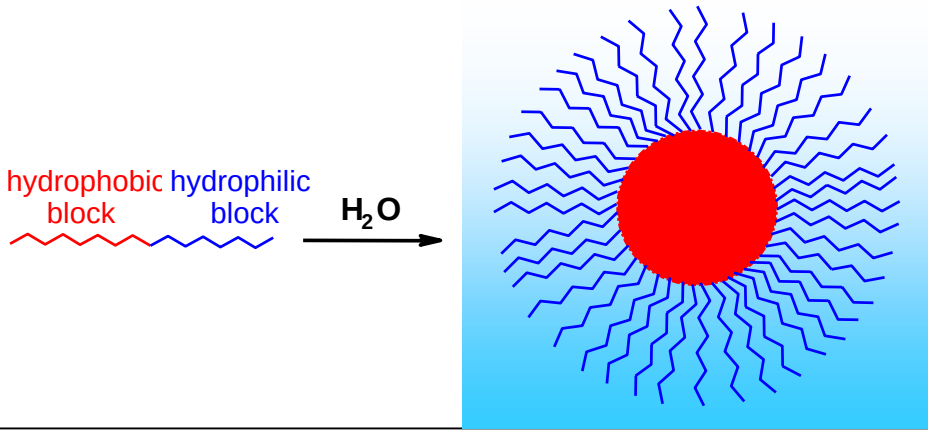
CH_3-$(EtOx)_{10}$-$(NonOx)_{10}$-OH



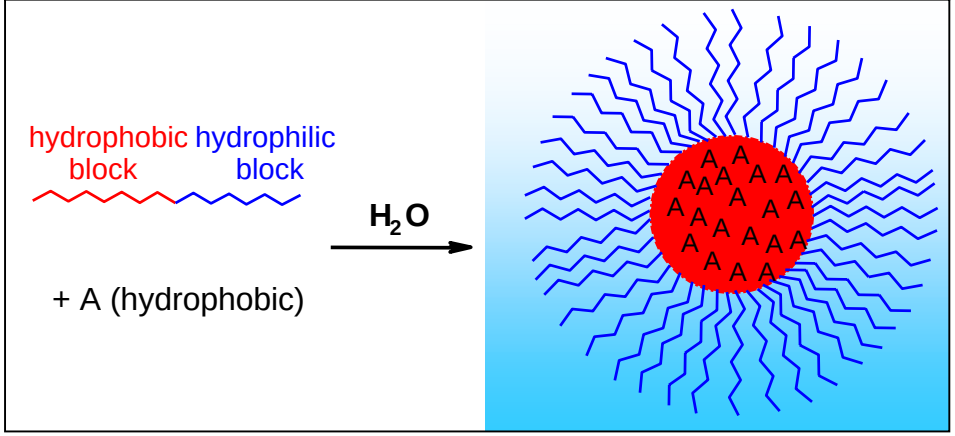
F. Wiesbrock, R. Hoogenboom, M. Leenen, S.F.G.M. van Nispen, M. van der Loop, U.S. Schubert, *in preparation*.

Diblock copolymers: Motivation

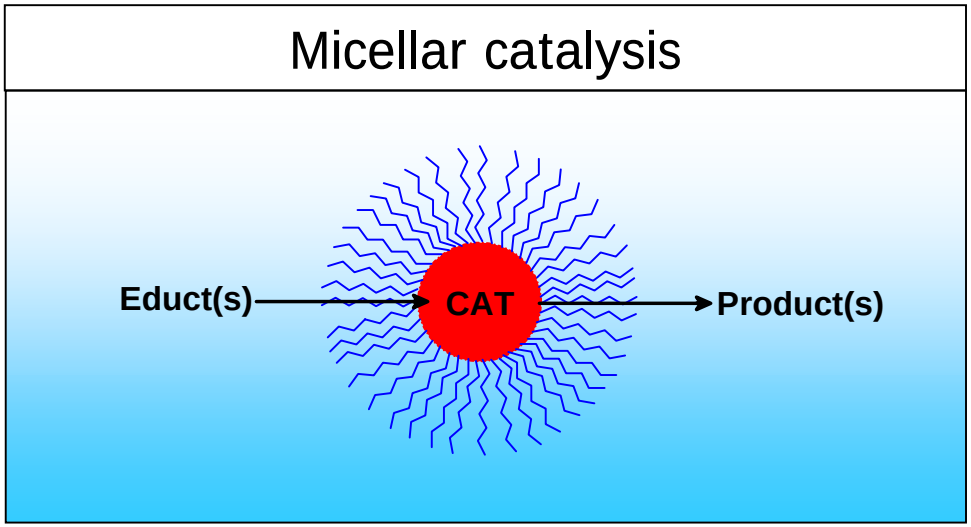
Formation of micelles



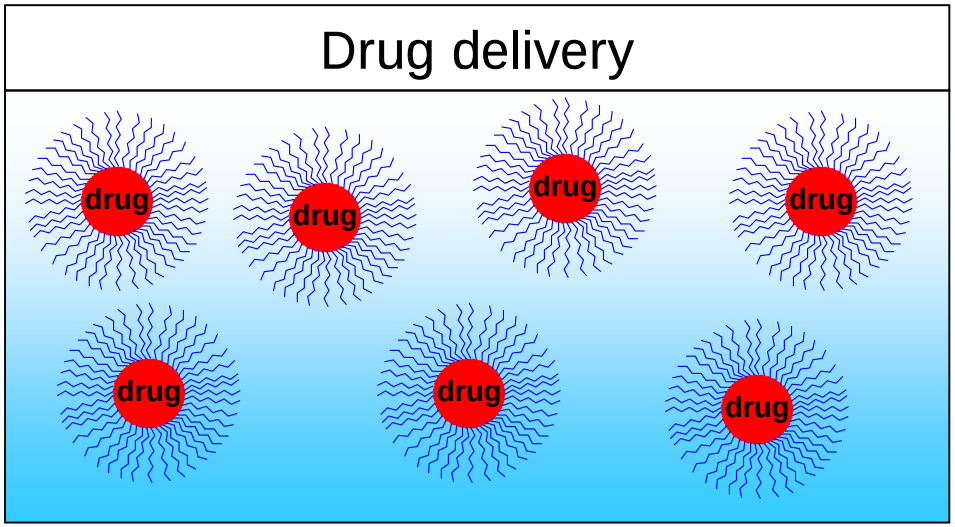
Micelles with hydrophobic agents



Micellar catalysis

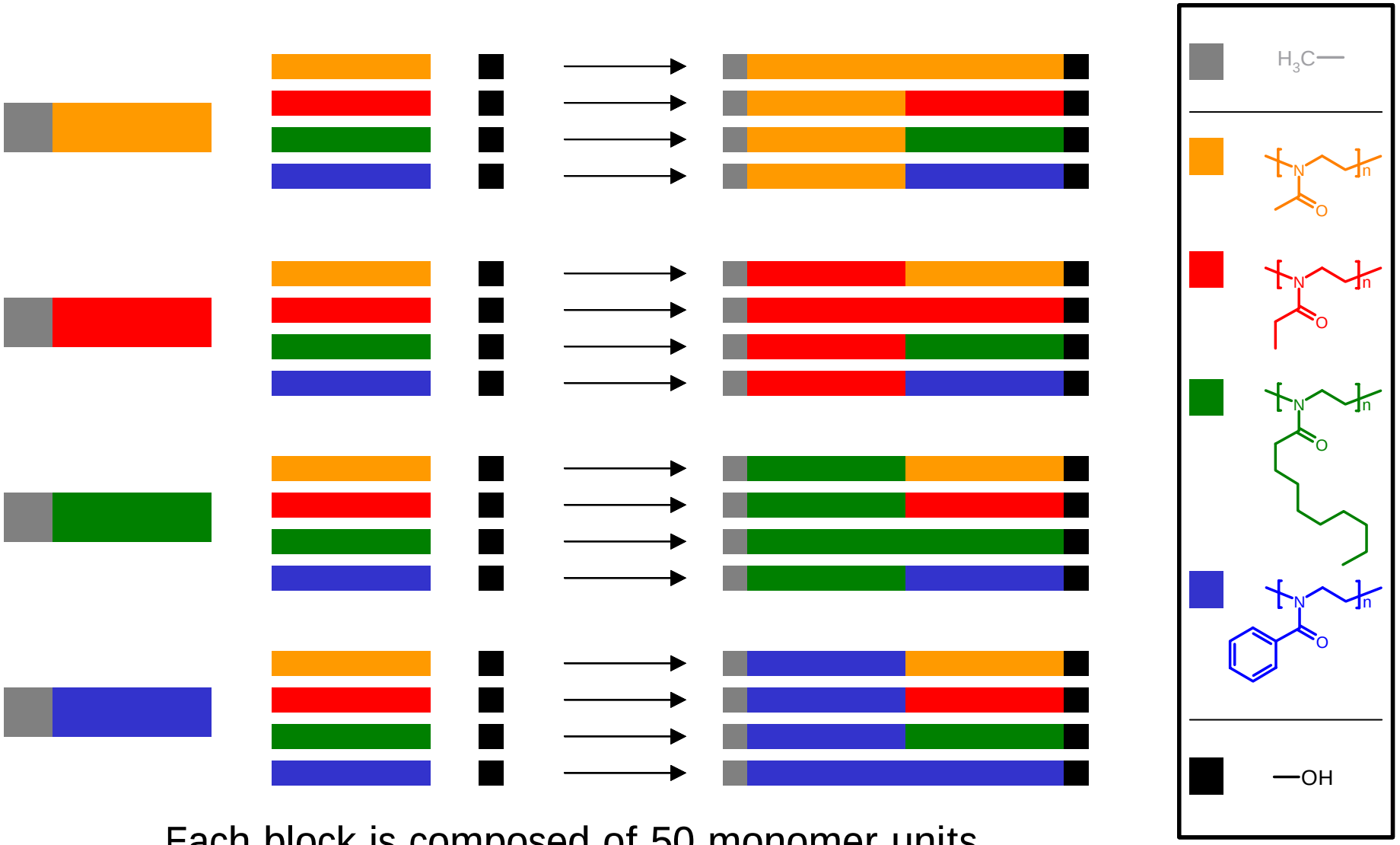


Drug delivery



Diblock copolymer library

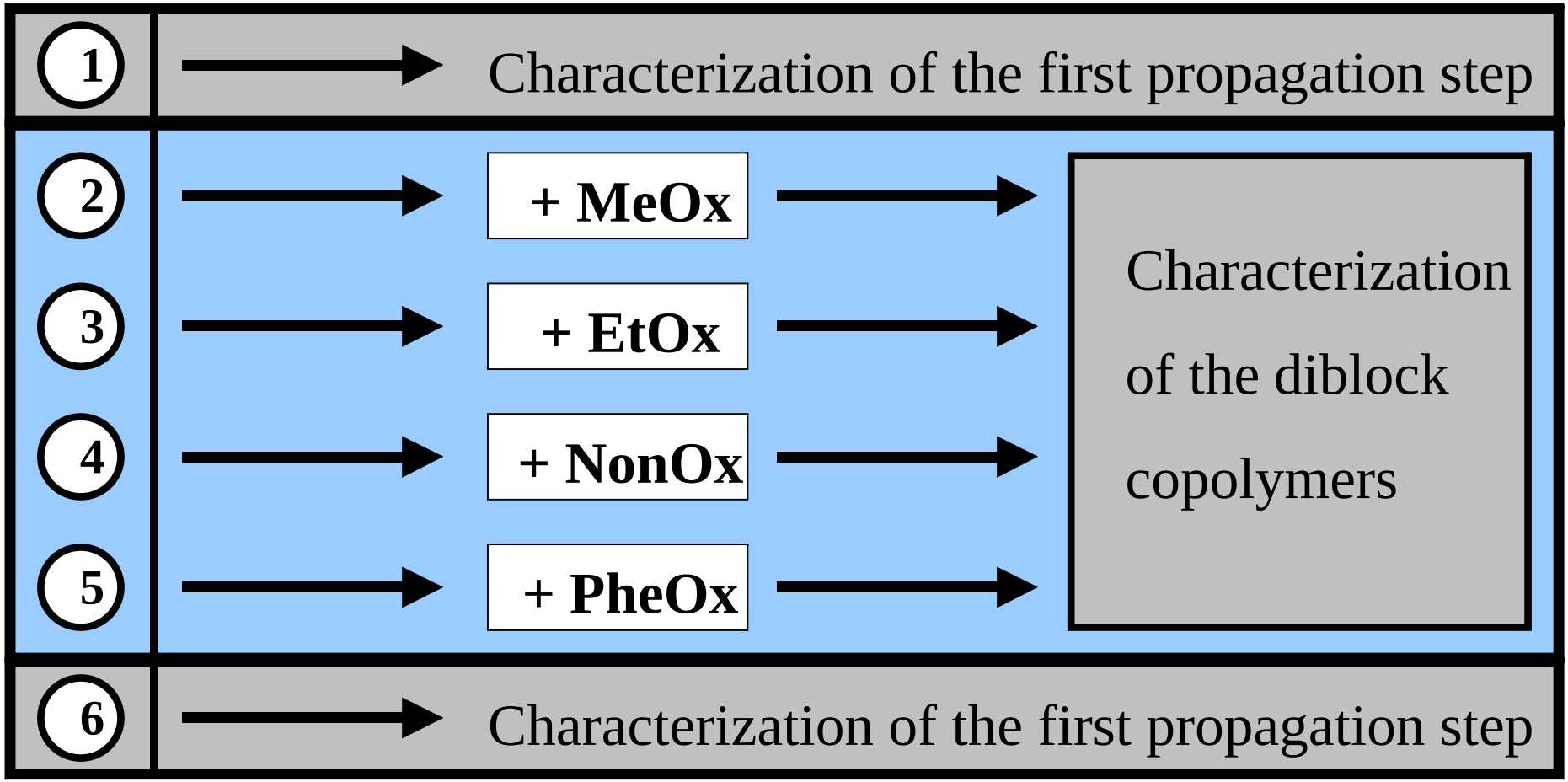
Synthesis of a 16-membered library of di block copolymers of the AB- and the AA-type



Each block is composed of 50 monomer units.

Copolymerization: Overview

General Procedure: Each first block prepared six times

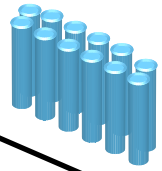


Synthesis: Overview

Chemspeed Platform or fumehood (*)

Single-mode microwave reactor

1. Preparation of a stock solution, transfer to the reaction vials

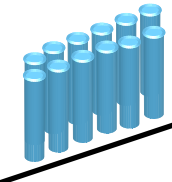


2. Synthesis of the first block

3. Addition of the second monomer

4. Incorporation of the second block

5. Analysis of the (set of) diblock copolymers

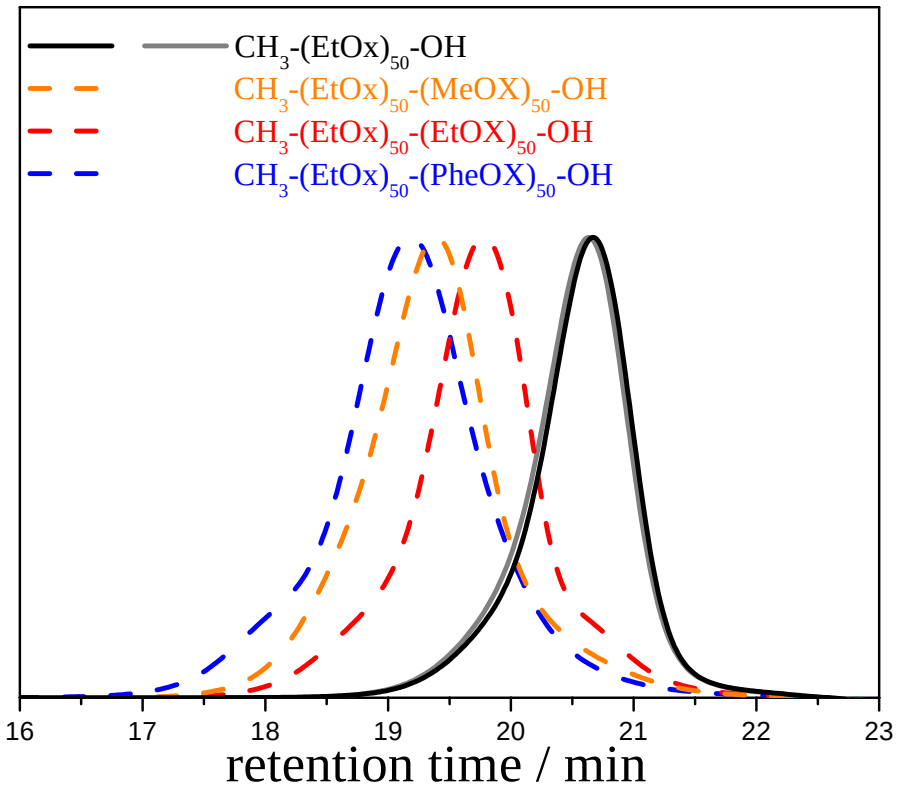


(*) depending on the number of experiments

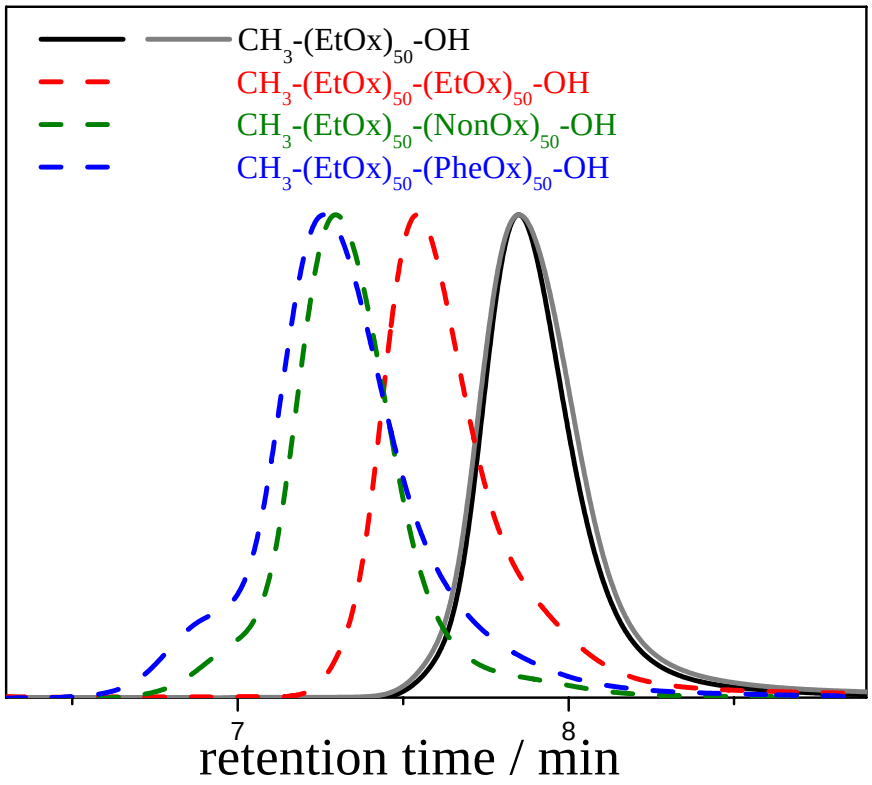
GPC characterization

Poly(2-ethyl-2-oxazoline) as first block; GPC measurements

in DMF



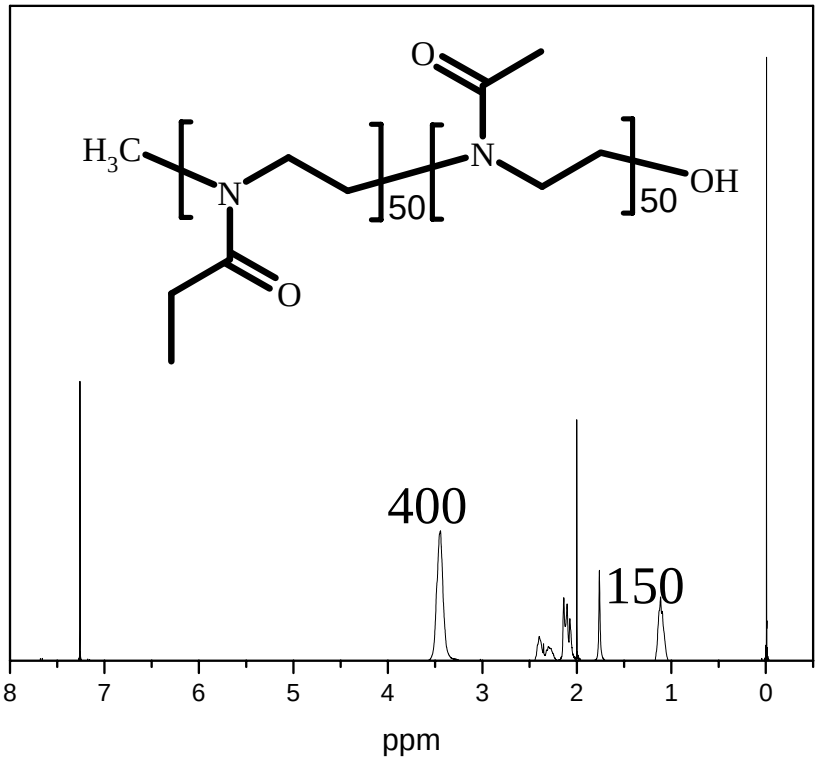
in $CHCl_3$

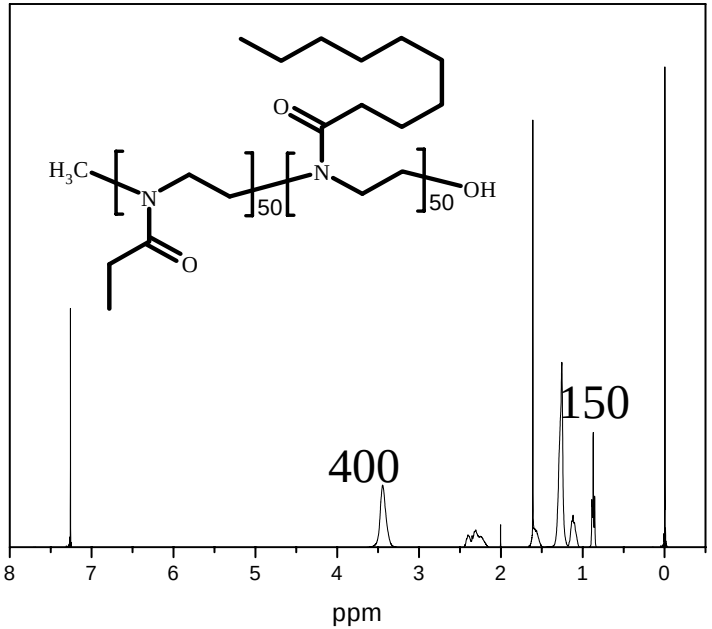


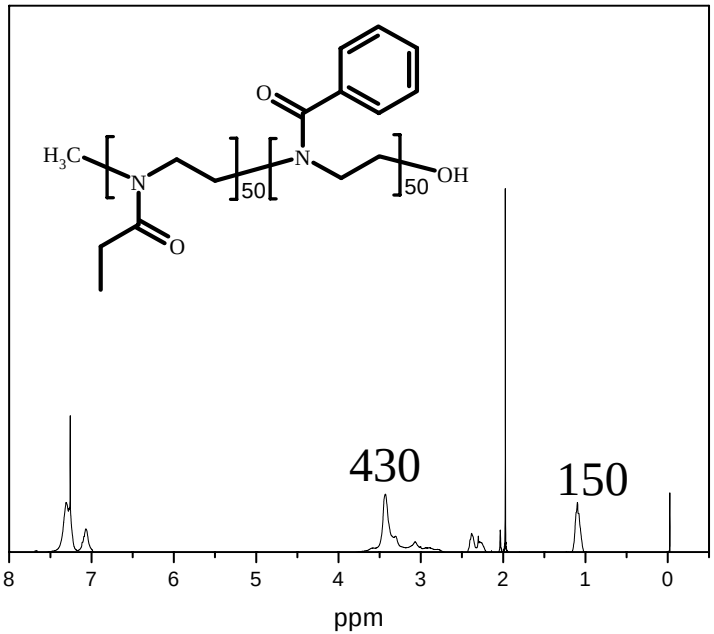
Reliable number average molecular weights can be obtained only for the mono block polymers and the diblock copolymers of the AA-type. Diblock copolymers of the AB-type can be characterized by ^{1}H-NMR (combined with the analysis of the first block by GPC measurements).

Diblock copoly(2-oxazoline)s:

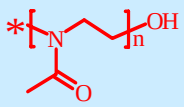
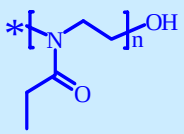
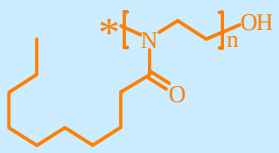
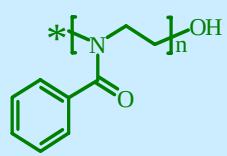
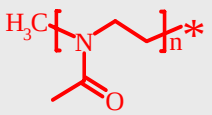
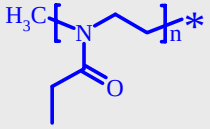
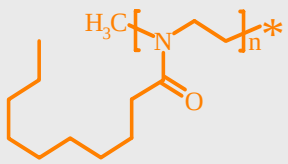
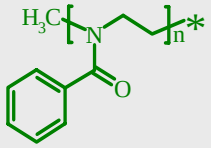
Measurements in $CDCl_3$







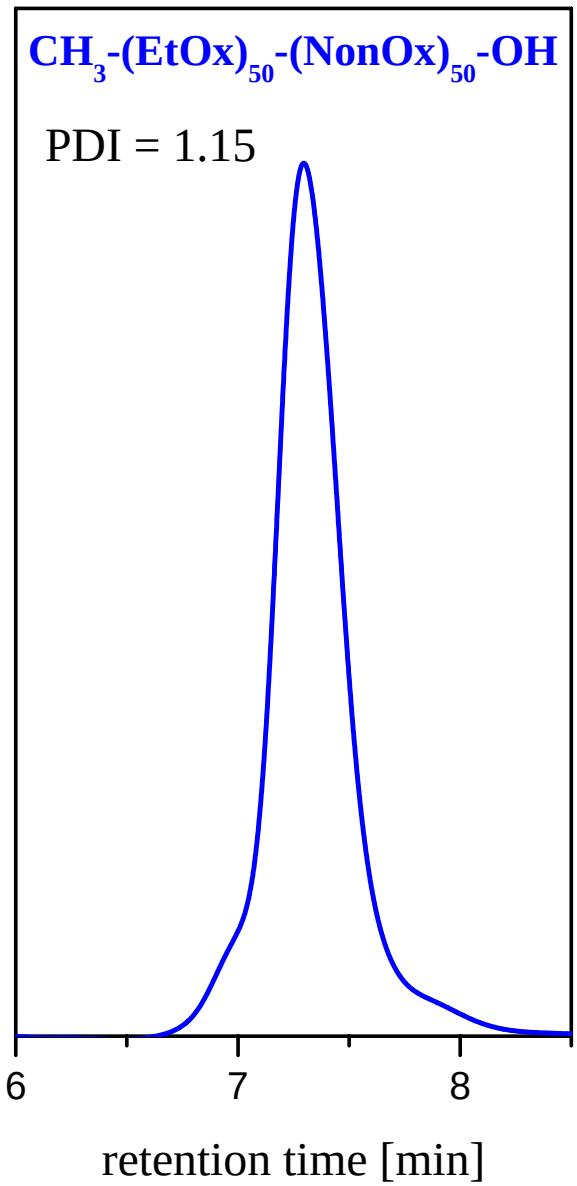
Block copolymer library

first block → / second block ↓				
	MeMe [4] p.t. 400+400 PDI ---/1.16	MeEt [4] p.t. 400+500 PDI ---/1.17	MeNon [4] p.t. 400+400 PDI ---/---	MePhe [4] p.t. 400+1800 PDI ---/1.25
	EtMe [4] p.t. 500+400 PDI ---/1.18	EtEt [4] p.t. 500+500 PDI 1.12/1.16	EtNon [4] p.t. 500+400 PDI 1.15(*)/---	EtPhe [4] p.t. 500+1800 PDI 1.27/1.19
	NonMe [2] p.t. 400+400 PDI ---/---	NonEt [2] p.t. 400+500 PDI ***1.70(*)***/---	NonNon [2] p.t. 400+400 PDI 1.43/---	NonPhe [2] p.t. 400+1800 PDI 1.14/---
	PheMe [3] p.t. 1800+400 PDI ---/1.18	PheEt [3] p.t. 1800+500 PDI 1.35/1.19	PheNon [3] p.t. 1800+400 PDI 1.28/---	PhePhe [3] p.t. 1800+1800 PDI 1.27/1.16

[n]: concentration of the respective monomers in mol/L; p.t. preparation time (in s);

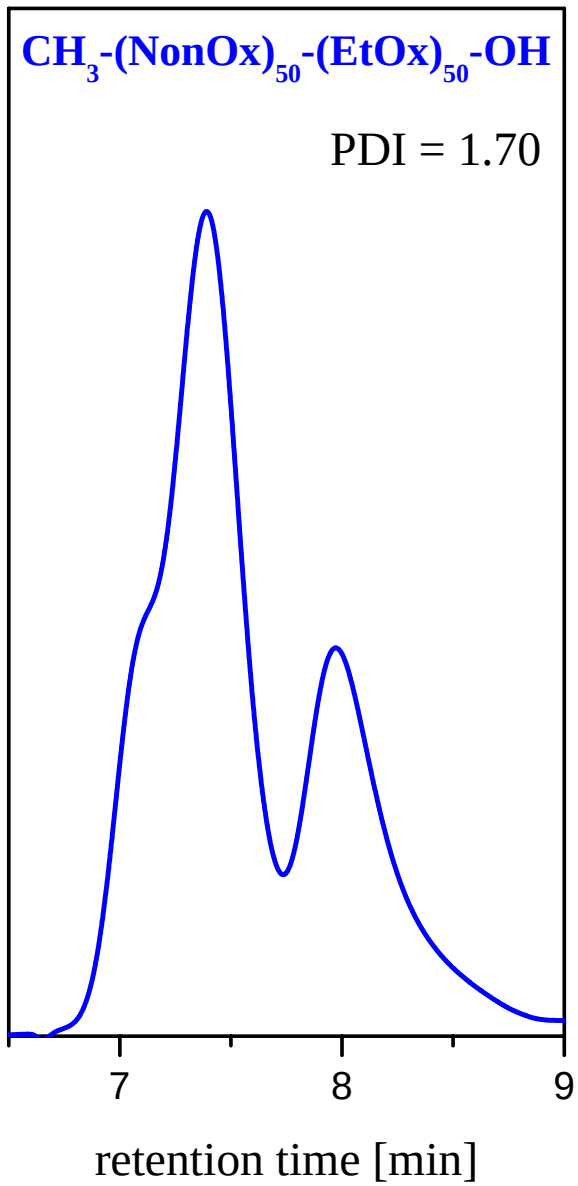
PDI values obtained from $CHCl_3$ /DMF solutions; (*): GPC traces on next slide

Diblock copoly(2-oxazoline)s



The order of incorporating the monomers into the polymer chain must be chosen carefully!

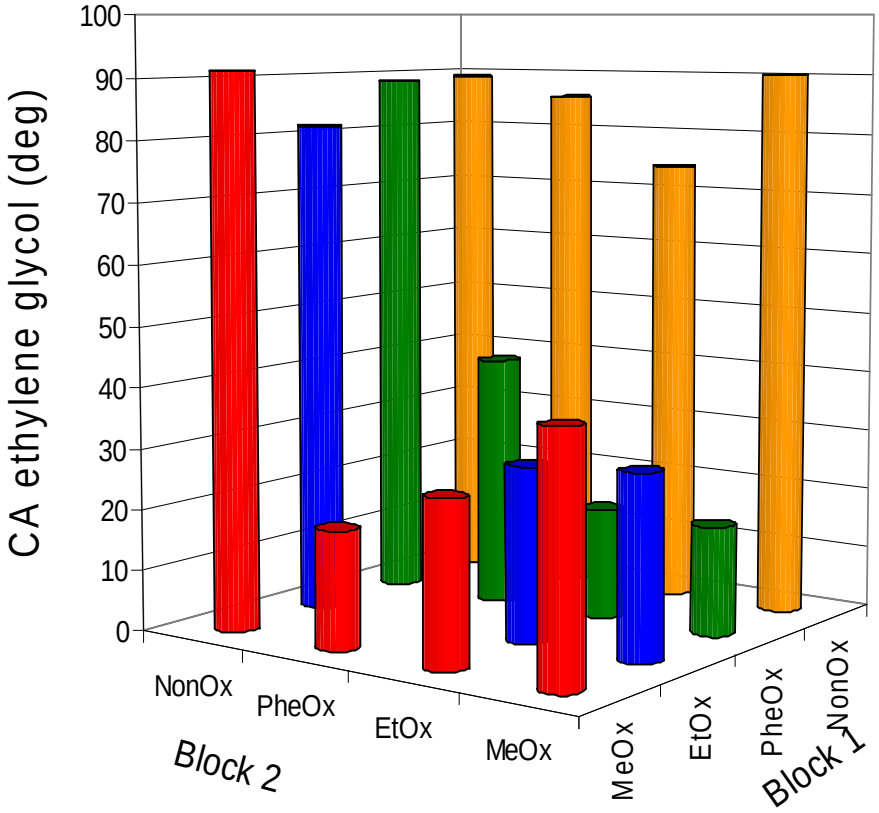
The findings in the course of the preparation of the NonOx-EtOx polymer were found to be reproducible and independent of the solvent (CH_3CN, CH_2Cl_2)



Contact-angle measurement

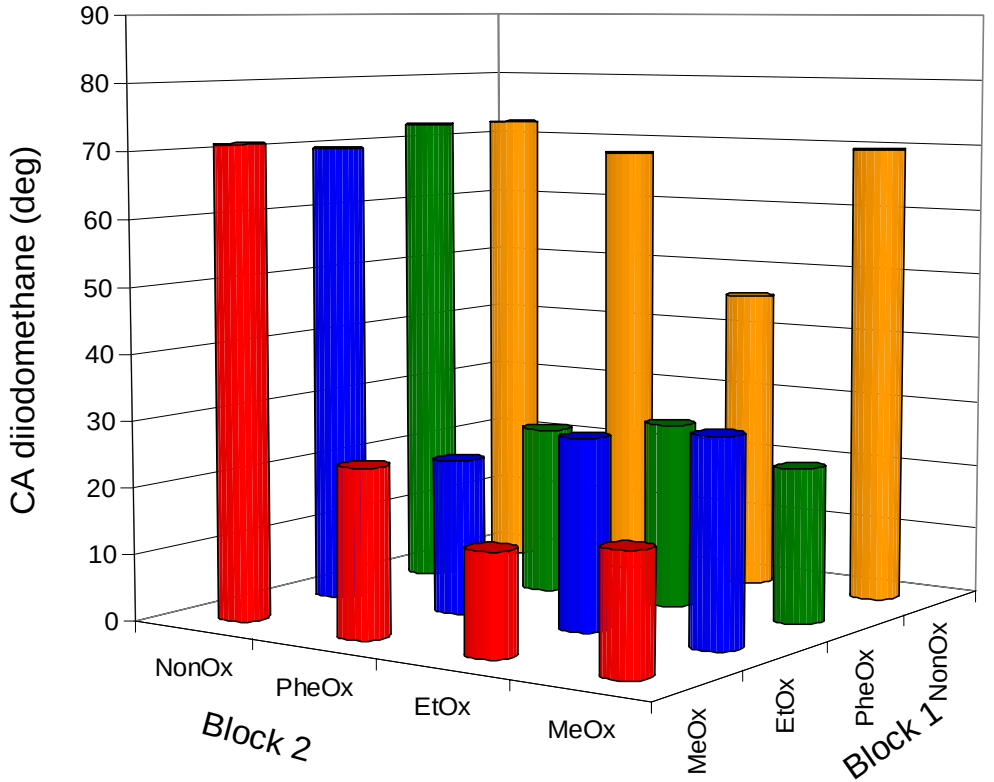
Polar test liquid: Ethylene glycol

4 Measurements per Contact Angle



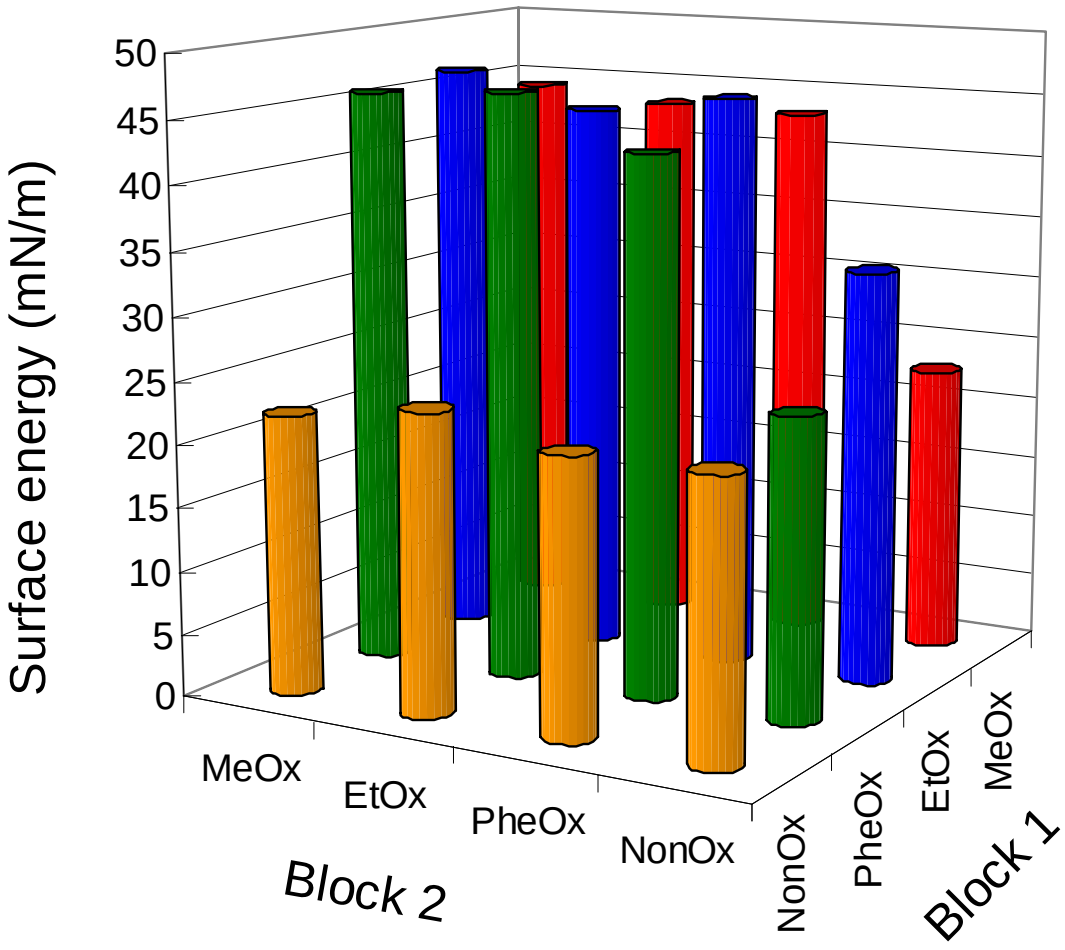
Apolar test liquid: Diiodo methane

4 Measurements per Contact Angle



S. Wijnans, B.-J. de Gans, F. Wiesbrock, R. Hoogenboom, U.S. Schubert, *Macromol. Rapid Commun.* **2004**, *25, in press*.

Contact-angle measurement



Nonyl chains preferentially orient to surface → lower surface energy

Result of 70 min measuring time (128 contact angles: saves time by factor 10)

Conclusions

A steadily growing number of polymer syntheses undergoes major improvements in terms of reaction times, purity and yields of the targeted product(s) under microwave irradiation.

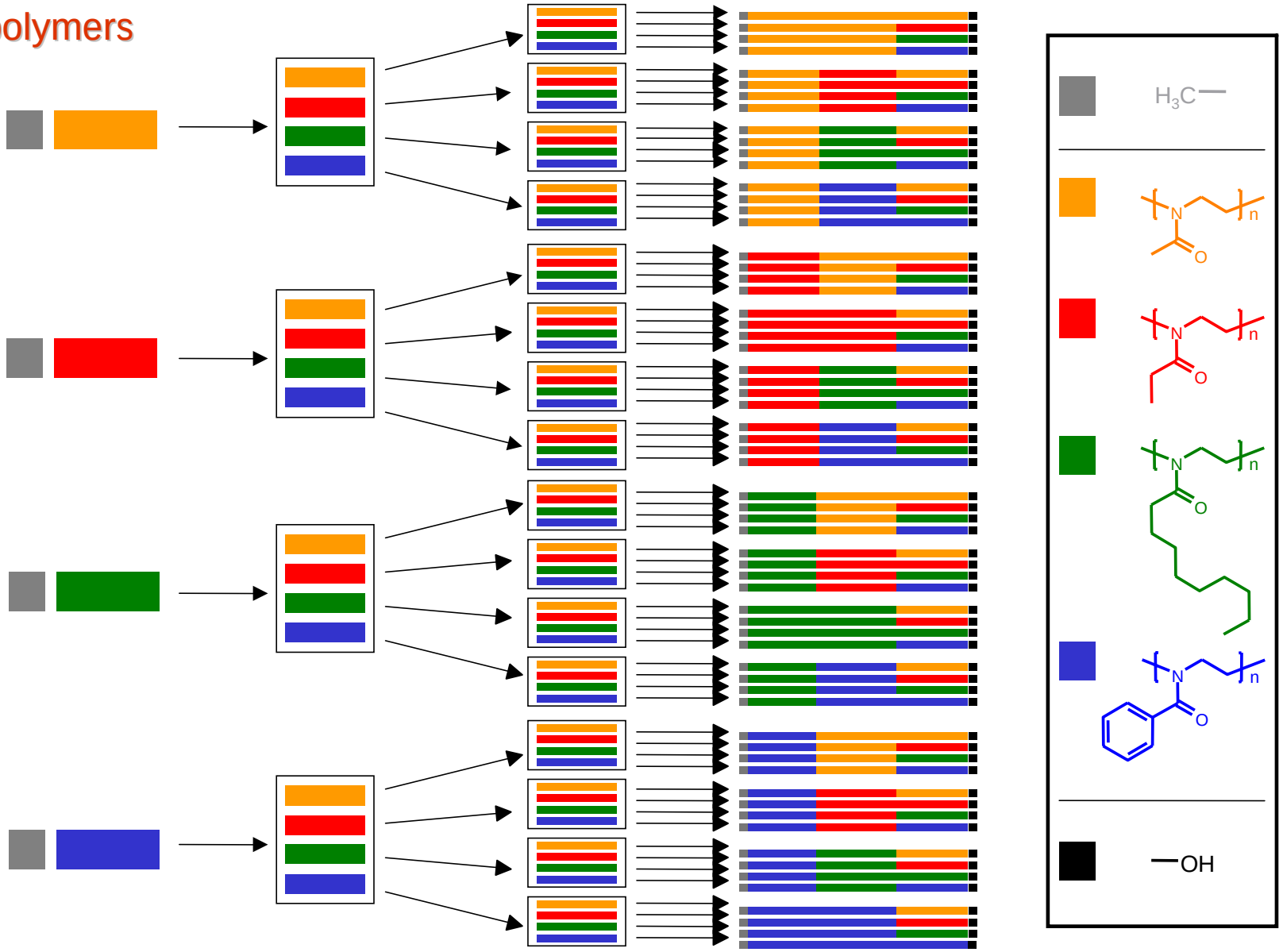
The living cationic ring-opening polymerization of 2-oxazolines undergoes remarkable accelerations under the high temperatures in the course of the microwave irradiation; first-order kinetics and livingness are maintained.

Diblock copoly(2-oxazoline)s can be prepared in a convenient 2-step process. For the incorporation of 50 monomers (per block) into the polymer chain, the total reaction times span the range from 14 minutes (EtOx-EtOx) to 80 minutes (PheOxPheOx).

The molecular weight distributions are narrow before and after the addition of the second monomer (except for the polymers that contain a poly (2-nonyl-2-oxazoline) as first block).

Outlook

64 Triblock copolymers



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