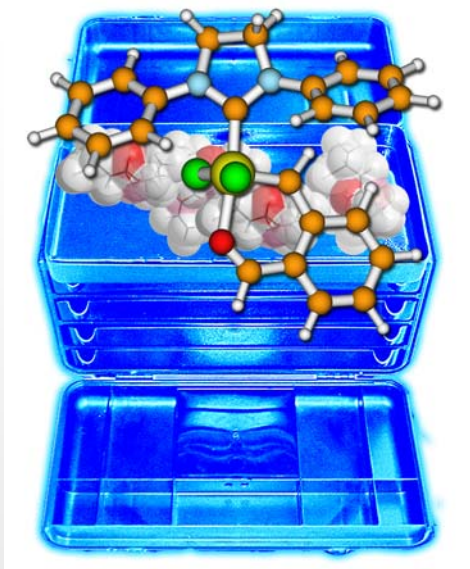


Functional Polymers designed for specific applications

or:
„News from our Metathesis Toolbox“



Presented by

Franz Stelzer, Christian Slugovc, Gregor Trimmel

(Institute for Chemistry & Technology of Organic Materials
Graz University of Technology „TUG“
Polymer Competence Center Leoben, „PCCL“)

at



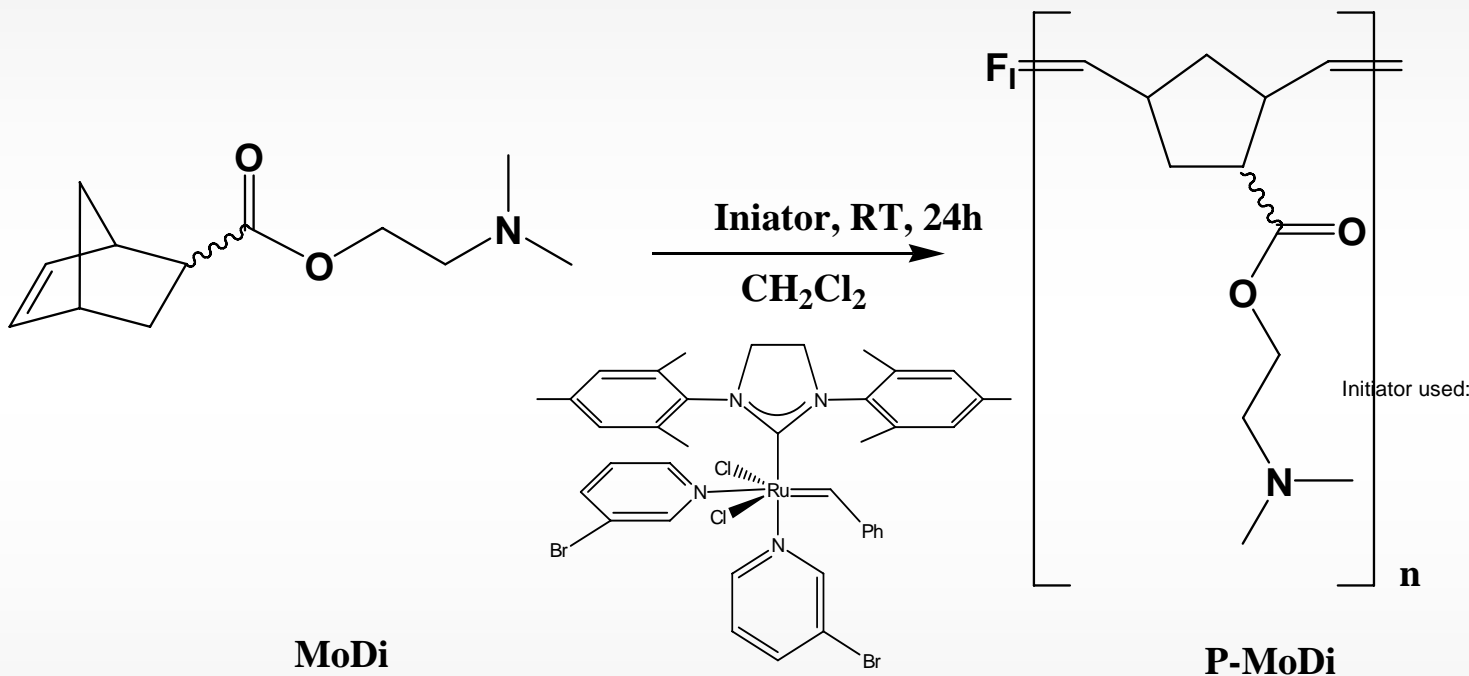
Agenda

- **Introduction and Motivation**
 - Functionalities
- **Structural Concepts**
 - Bulk-functionalization (functionalized homo-/co-polymers, compounding)
 - Single site functionalization (Endgroup functionalisation, low conc random copolymers)
- **Selected Examples**
 - Antimicrobial Polymers
 - Sensing polymers
 - Block-copolymers with well defined morphologies/particles
- **Conclusions**

Functions/Properties (selection)

- **Conductivity** – bulk property
- **Antimicrobial surfaces** – bulk/surface property
- **Luminescence/fluorescence**
 - chemical sensing: low conc copos/single site
 - OLEDs: bulk
 - Molecular markers: single site
- **Photochemical response** – bulk property

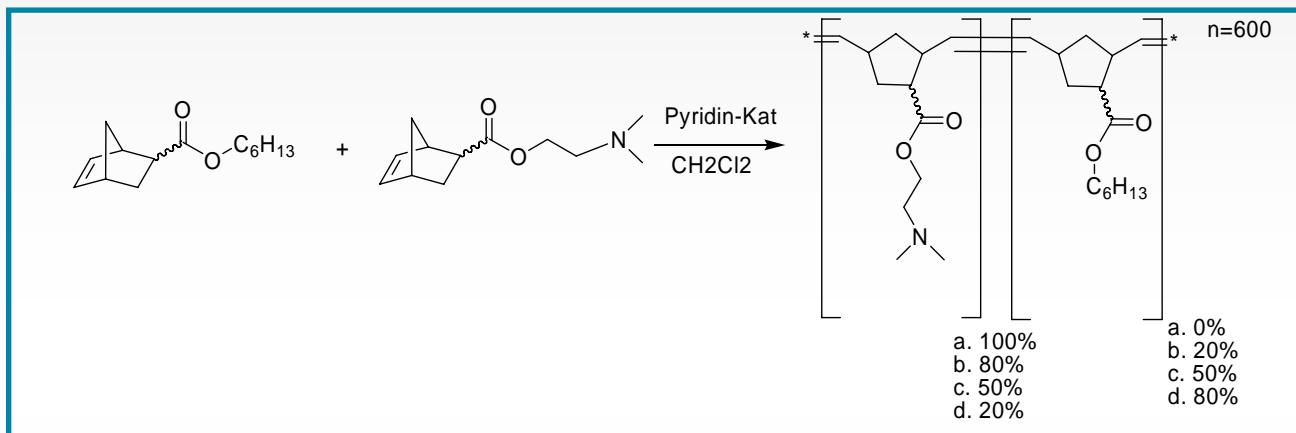
Synthetic scheme towards an antimicrobial polymer (ester as the anchor)



Chemical analyses: NMR, FTIR, DSC, TGA,
(GPC, MALDI-TOF)

Copolymers and alkylated/quarternarized Copolymers

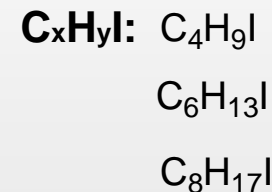
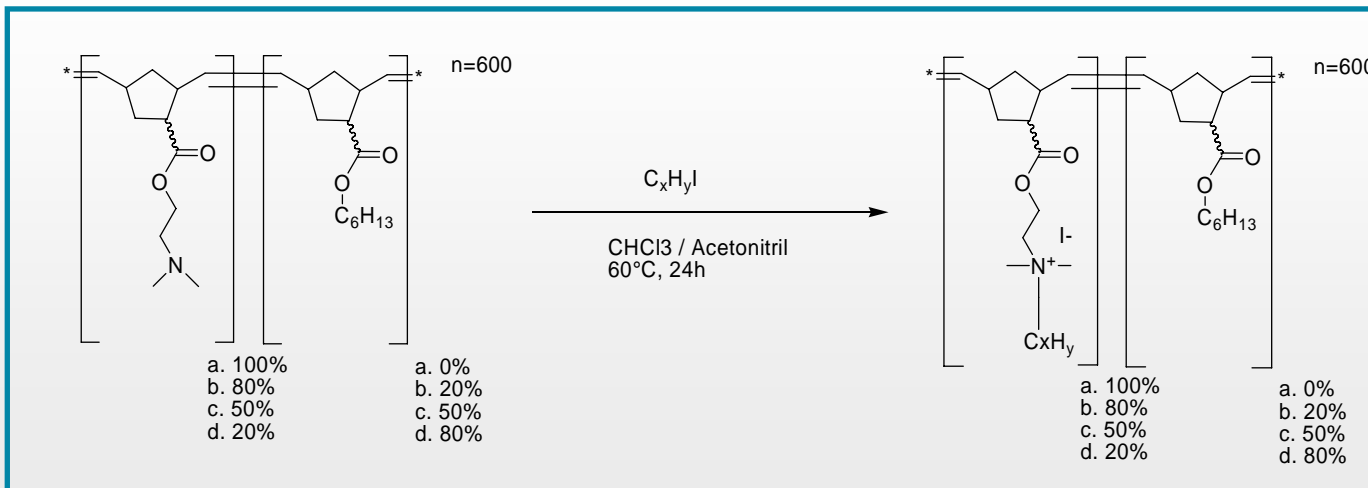
Copolymerization („high conc random“):



Characterization:

- NMR
- FTIR
- DSC
- Contact angle

Alkylation (Quarternization of the amino group) :



Antimicrobial Compounds

Compounding:

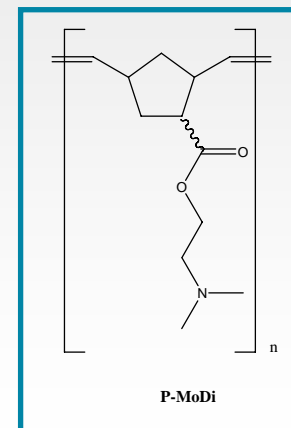


Thermo-Haake Minilab

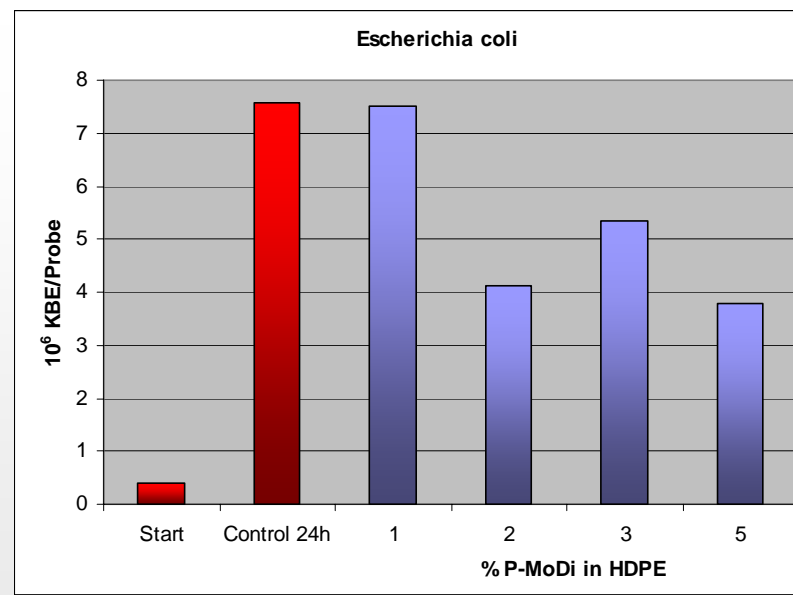
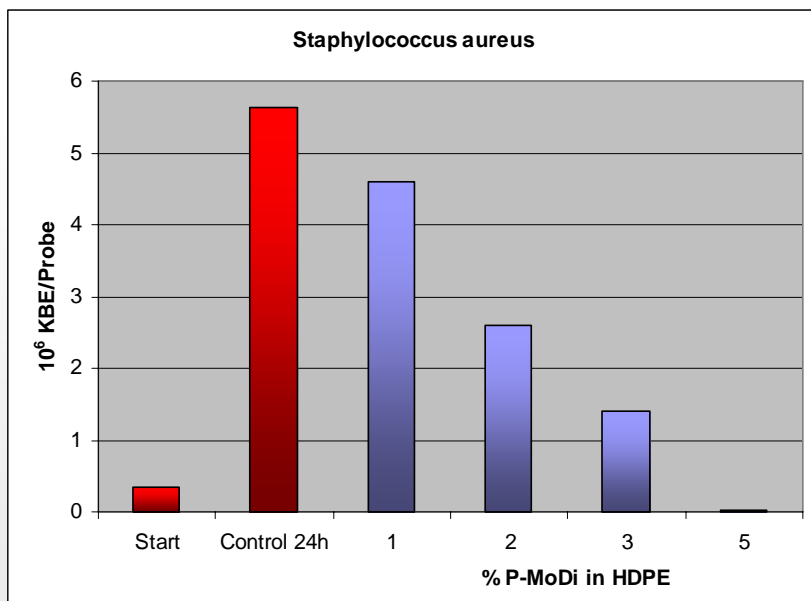
HDPE-Compounds containing

- 1 % P-MoDi
- 2 % P-MoDi
- 3 % P-MoDi
- 5 % P-MoDi

Compounding at 190°C



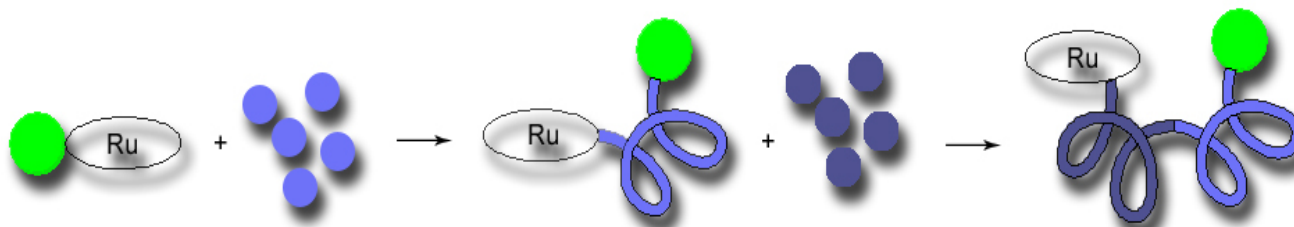
Antimicrobial properties:



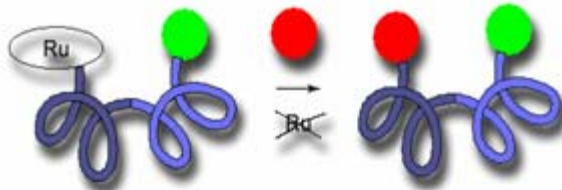
Single-site (end group-) Functionalisation of the Polymers



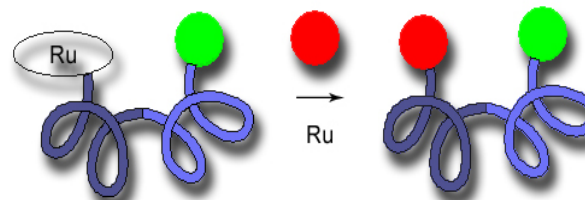
Mono-function: Functionalized Initiator



Double function:

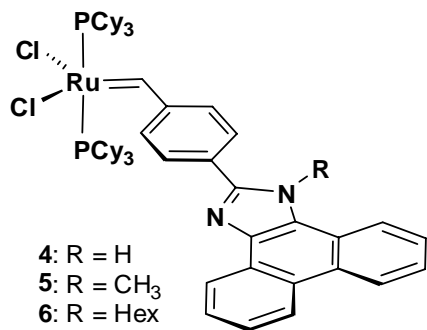
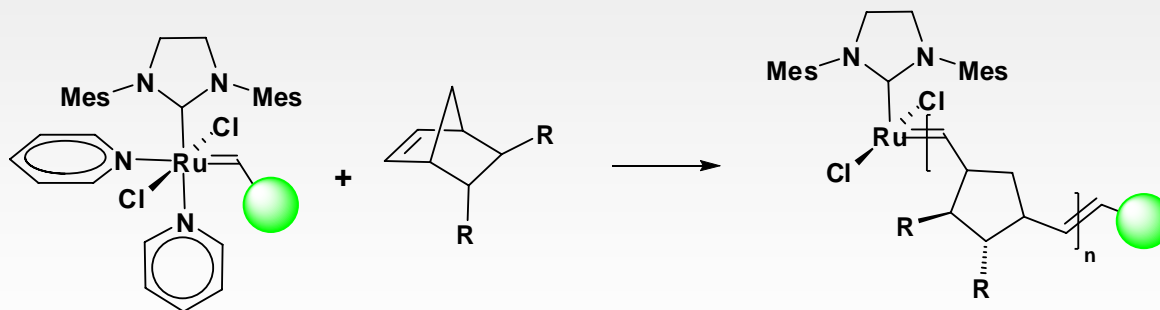


Termination

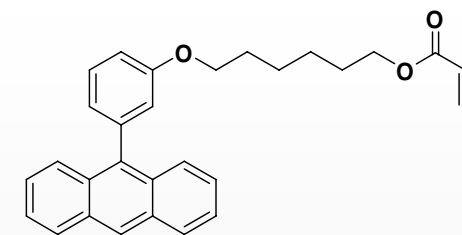


Cross Metathesis

Example 2: Modified Initiator /Endcapping agent



Modified Initiators



New endgroup
functionalization agents

Bielawski, C.; Louie, J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 12872.

Gomez, F. J.; Chen, R. J.; Wang, D.; Waymoth, R. M.; Dai, H. *Chem. Commun.* **2003**, 190.

Castle, T. C.; Hutchings, L. R.; Khosravi, E. *Macromolecules* **2004**, *37*, 2035.

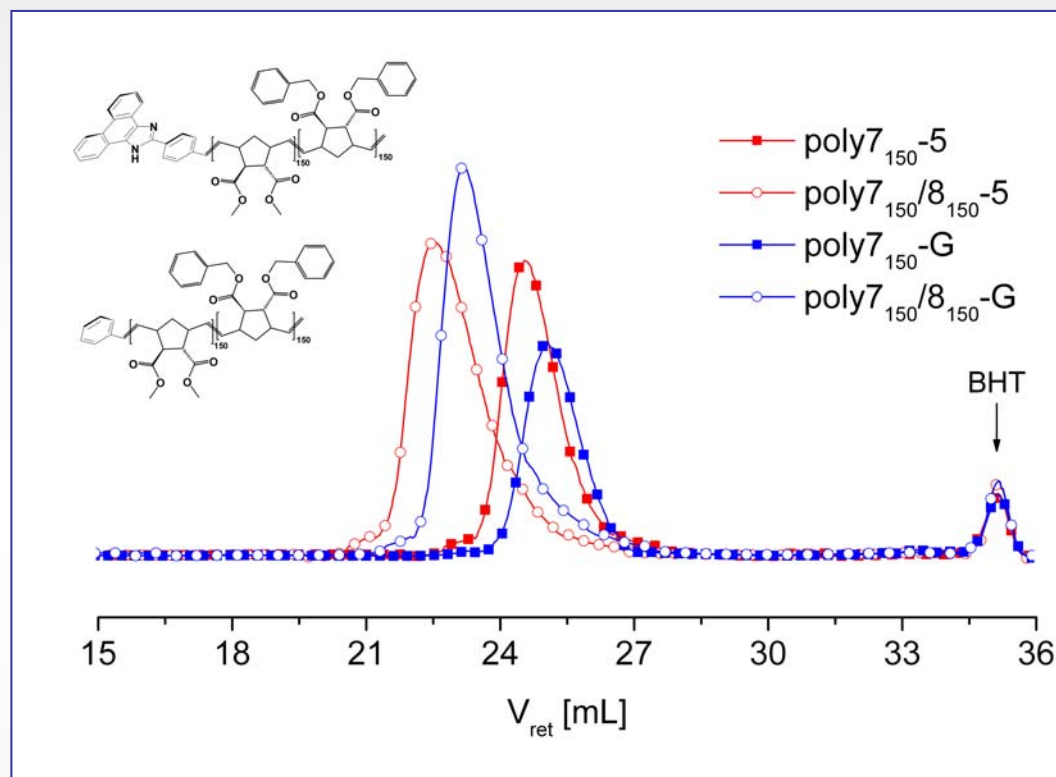
Burtscher, D.; et al. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 6136.

Noormofidi, N.; Slugovc, C. *Macromol. Chem. Phys.* **2007**, *208*, 1093.b

Precise Placement of Functionalities – functionalized Initiators

Oligomer or Polymer	Initiator (eq.) : Monomer(s) (eq.)	PDI	M _n (g/mol)
oligo7 ₁₀ -4	4 (1) : 7 (10)	1.40	2600
poly7 ₃₀₀ -4	4 (1) : 7 (300)	1.19	77000
poly7 ₃₀₀ -5	5 (1) : 7 (300)	1.18	78000
poly7 ₃₀₀ -6	6 (1) : 7 (300)	1.16	78700
poly7 ₃₀₀ -G	G (1) : 7 (300)	1.12	67130

Oligomer or Polymer	Initiator (eq.) : Monomer(s) (eq.)	PDI	M _n (g/mol)
poly7 ₁₅₀ /8 ₁₅₀ -5	5 (1) : 7 (150)	1.14	53700
	then 8 (150)	1.26	84300
poly7 ₁₅₀ /8 ₁₅₀ -G	G (1) : 7 (150)	1.09	39600
	then 8 (150)	1.24	63300



Homopolymers and Copolymers, with low PDI

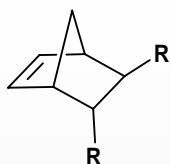


Properties of the initiator (activity, „Livingness“) retained !

Daniel Burtcher, Poster at this event!!

Living Polymerization with Indenylidene Type Initiators

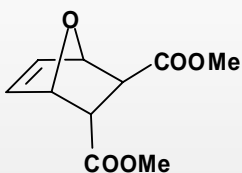
Polymer	Yield (%)	PDI	M_n (g/mol)
polyB ₃₀₀ -A	63	1.07	45 000
polyC ₃₀₀ -A	85	1.06	65 000
polyD ₃₀₀ -A	66	1.07	49 000
polyE ₃₀₀ -A	77	1.09	50 000



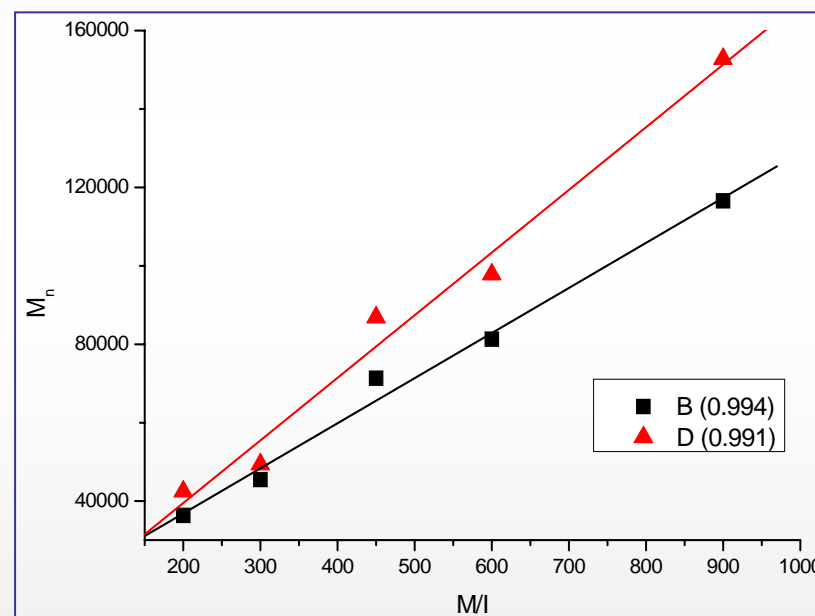
B: R = COOMe

C: R = COOBn

D: R = CH₂OEt



E

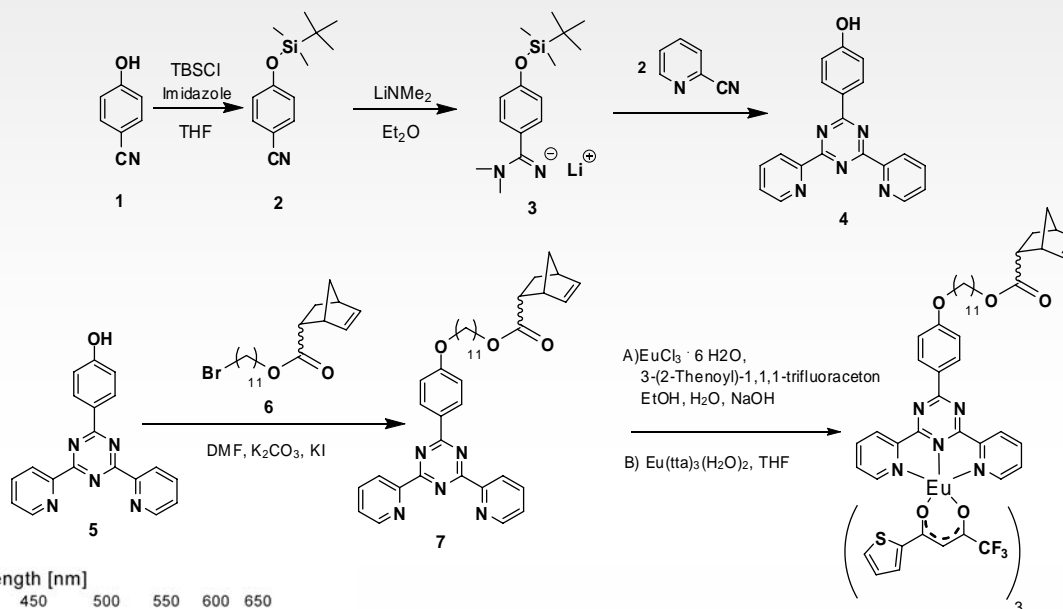


May be considered „living“

Burtscher, D.; et al. submitted.

Water-sensitive dye – incorporated into hydrophilic block

Example 4 :



Incorporated into
ROMP-Homo- or
Co-polymer

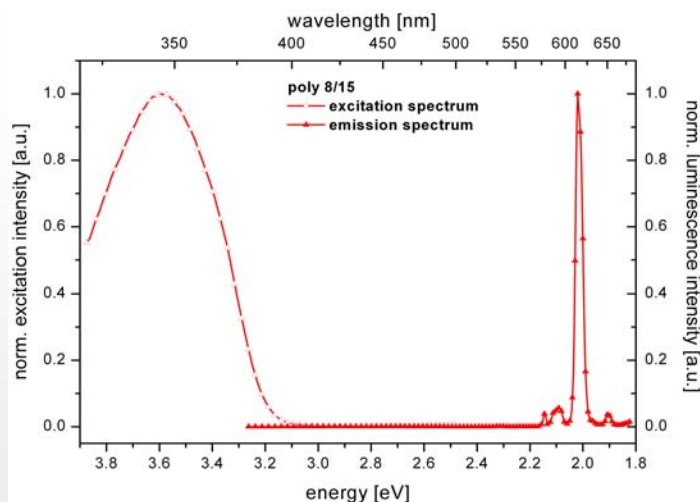


Figure 1: Excitation and luminescence spectra of **poly 8/15** in thin film ($\lambda_{ex} = 360$ nm)

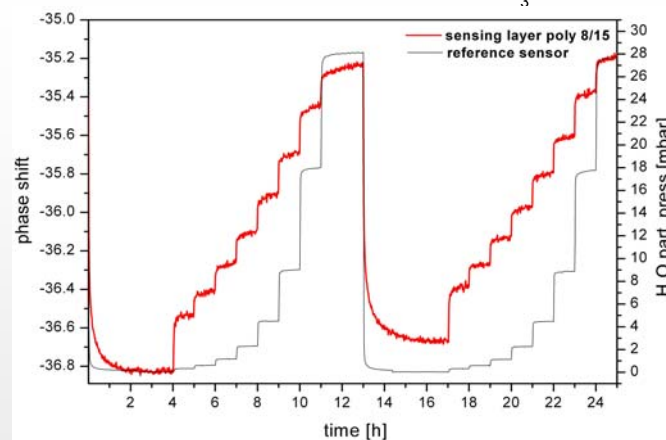
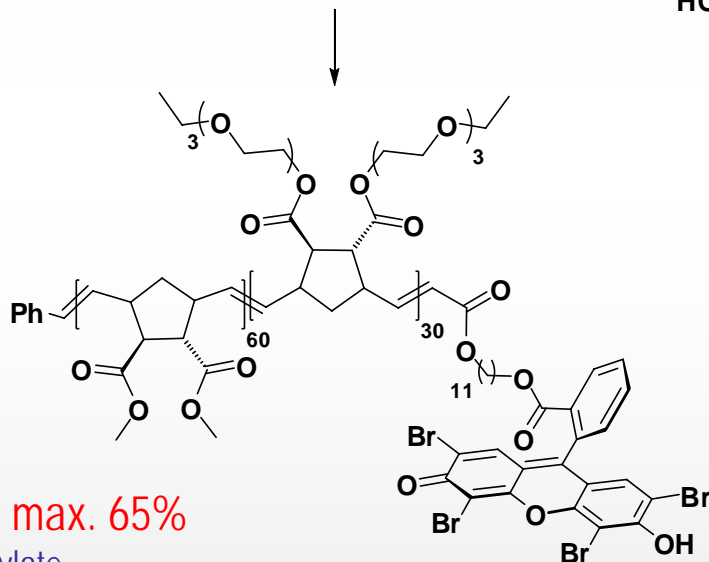
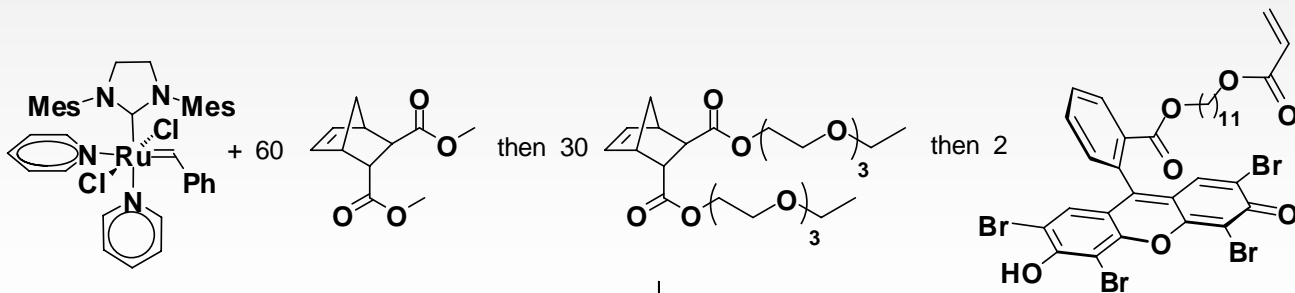
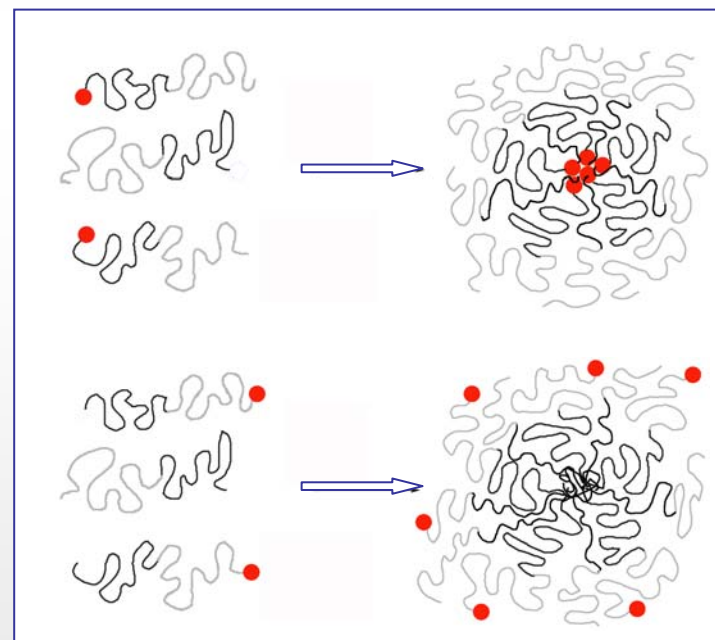


Figure 2: Response curves of the sensing layer **poly 8/15** (red) and a reference sensor (black) upon water exposure.

Example 5: Precise Placement of Functionalities - Eosin in Block-Copolymer



Micelles e.g. in MeOH



Capping efficiency: max. 65%

2 eq. of the acrylate

Reaction time 1h, RT

Lexer, C.; Sandholzer, M. unpublished.

Sandholzer, M.; Lex, A.; Trimmel, G.; Saf, R.; Stelzer, F.; Slugovc, C. *J. Polym. Sci. Part A* 2007, 45, 1336.

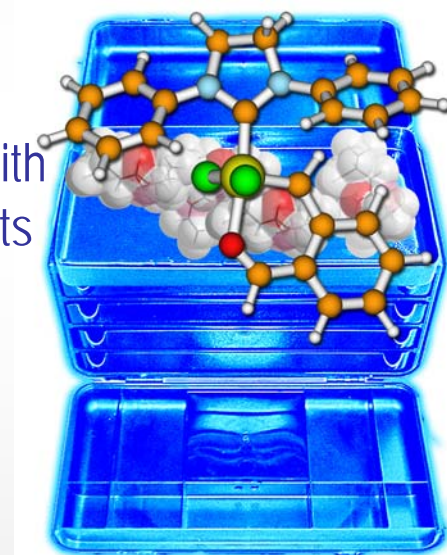
Summary



Synthesis of functional bulk-polymers easily possible with Metathesis Toolbox
(functional monomers)

Single-site functionalisation is possible via Living ROMP
with N-donor functionalized carbene-initiators together with
Acrylates as convenient end-group functionalizing agents

Functionalized block-copolymers with well defined
block size and particle morphology are easily accessible



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