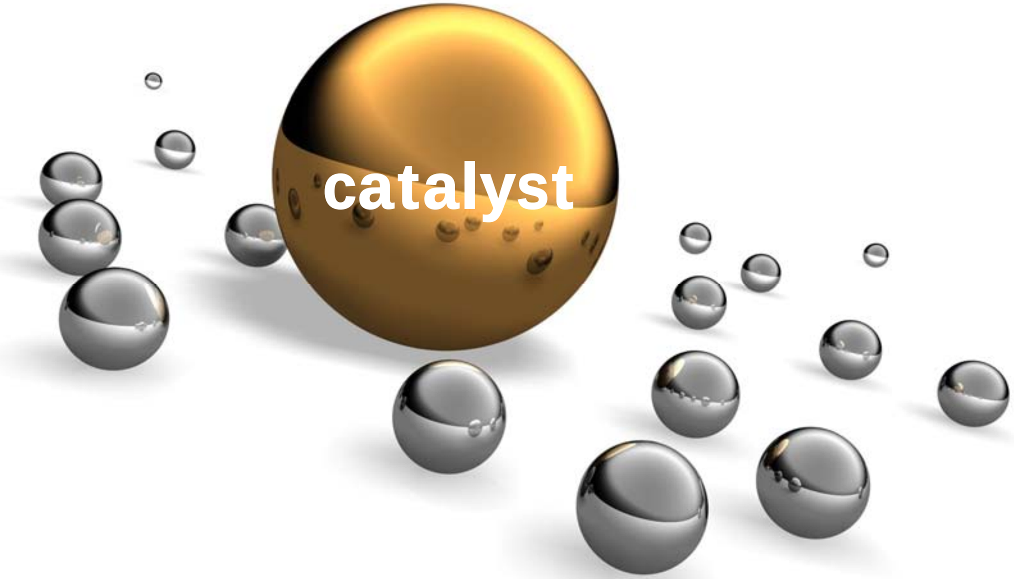
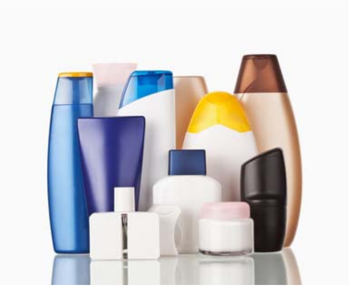
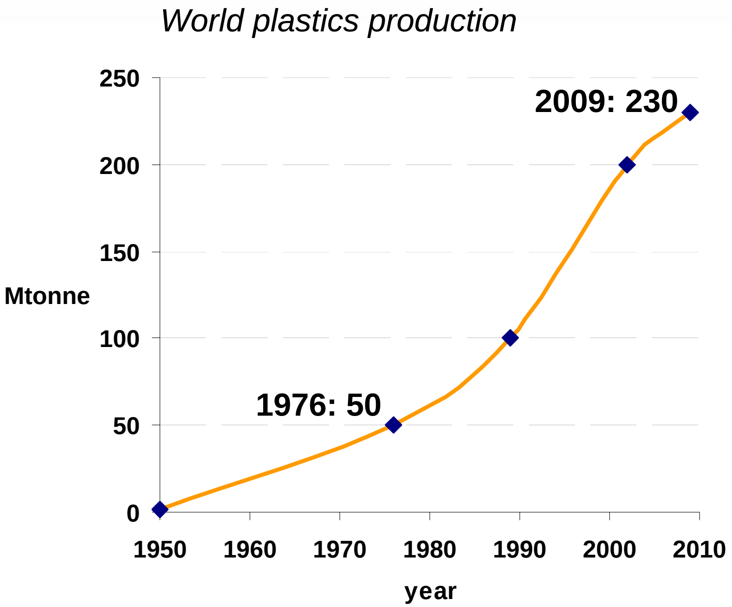
Metallkatalysatoren für Depolymerisationsprozesse



Stephan Enthaler

Introduction





Grow rate: ~9% p.a.

"Any future scenario where plastics do not play an increasingly important role in human life therefore seems unrealistic."

A. L. Andrady, M. A. Neal, *Phil. Trans. R. Soc. B* **2009**, *364*, 1977.

PlasticsEurope 2010

Introduction

Backside of the success (I):

- Plastics derived mainly from petrochemicals
- 4% of the annual petroleum production
- Additional 3-4% for manufacture energy

Backside of the success (II):

- plastic production: 55 Mtonnes (2007, EU)

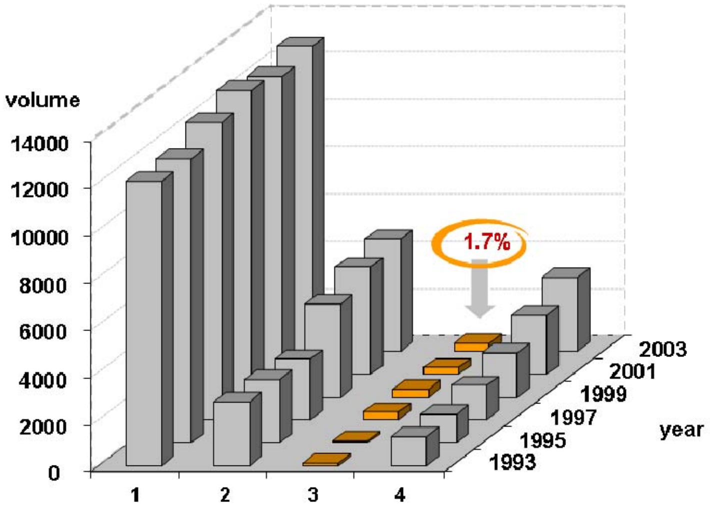
vs.

- end-of-life-plastics: 25 Mtonnes (2007, EU)

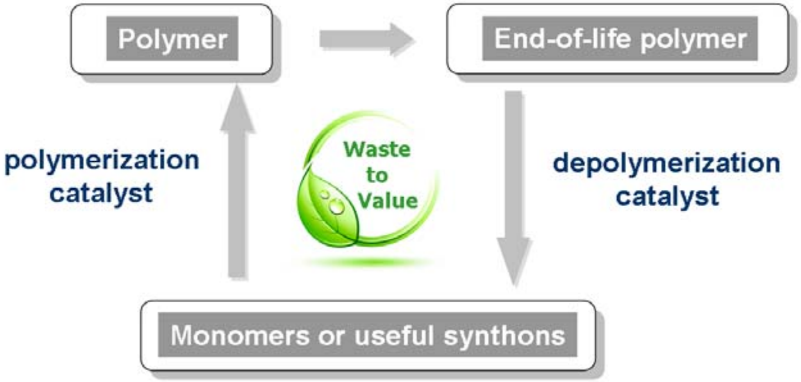
R. C. Thompson, S. H. Swan, C. J. Moore, F. S. vom Saal, *Phil. Trans. R. Soc. B* **2009**, *364*, 1973.

Introduction

Figure 2. Volumes of plastic waste (Western Europe)



1: landfill
2: energy recovery (thermal recycling)
3: feedstock recycling
4: mechanical recycling (downcycling)



Ru: 150€/mol
Rh: 2484€/mol
Pd: 1460 €/mol

Zn

12€cent/mol

Fe

0.5€cent/mol

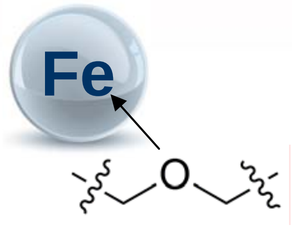
Depolymerization requirements

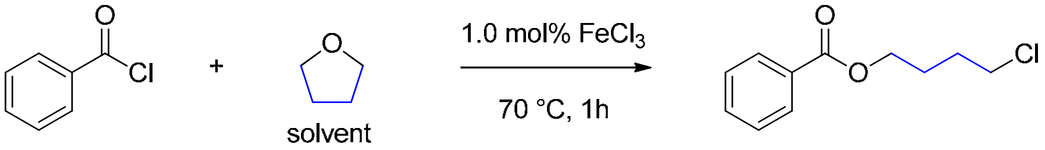
- abundant and cheap catalyst/reagents
- robust
- low toxicity
- non-inert conditions
- low-temperature
- solvent-free

- Iron Catalysis in Organic Chemistry (Ed.: B. Plietker), Wiley-VCH, **2008**.
- Zinc Catalysis – Application in Organic Synthesis (Ed.: S. Enthaler, X.-F. Wu), Wiley-VCH, **2014**.

Depolymerization of Polyethers

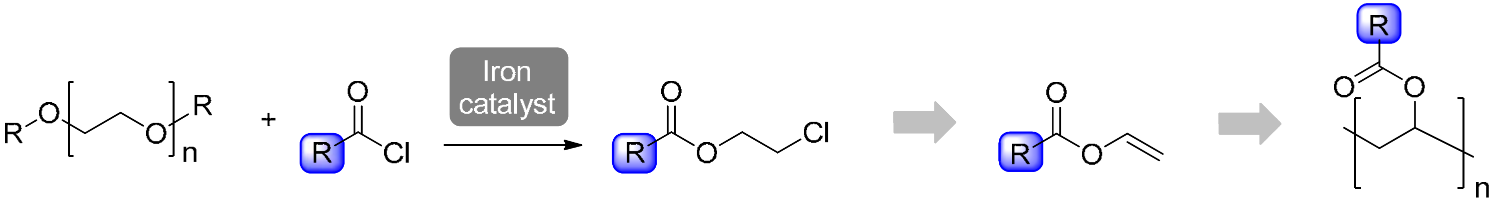
Polyether: Polyethylene glycol (24.000.000 t/a)
Polypropylene oxide (6.600.000 t/a)
Polytetrahydrofuran (250.000 t/a)





yield: >99%

Transfer of the concept

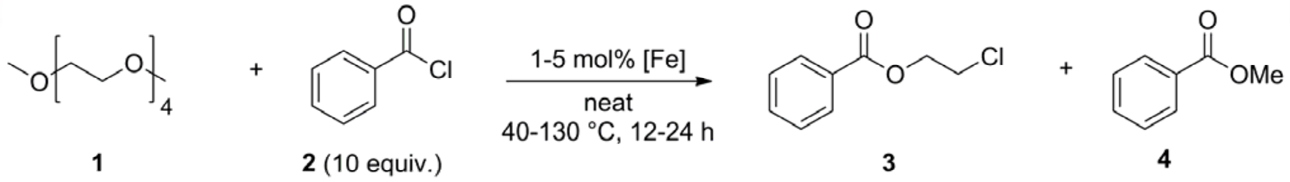


Polyethers

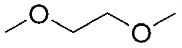
Monomers

Polymers

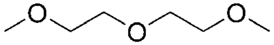
Depolymerization of Polyethers



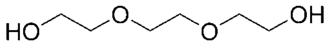
Entry[a]	Iron source (mol%)	T [°C]	Yield (3) [%][b]
1	--	130	<1
2	$FeCl_2 \cdot 4H_2O$ (5)	130	**87**
3	$FeCl_3$ (5)	130	81
4	$FeBr_3$ (5)	130	69
5	$Fe(ClO_4)_2 \cdot H_2O$ (5)	130	71
6	$Fe(ClO_4)_3 \cdot 4H_2O$ (5)	130	73
7	$FeCl_2 \cdot 4H_2O$ (2.5)	130	82
8	$FeCl_2 \cdot 4H_2O$ (1.0)	130	68
9	$FeCl_2 \cdot 4H_2O$ (5)	100	86
10	$FeCl_2 \cdot 4H_2O$ (5)	80	69



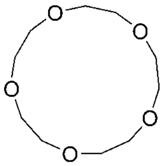
Yield: 79 %



Yield: 81 %



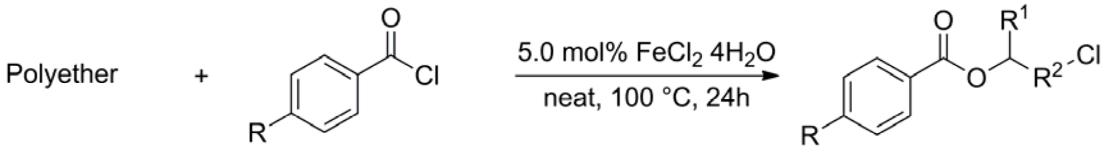
Yield: 73 %

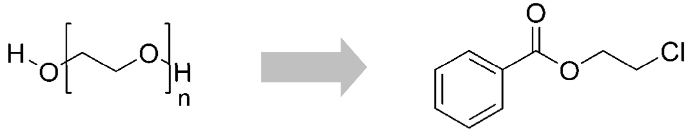


Yield: 82 %

- S. Enthaler, M. Weidauer, *ChemSusChem* **2012**, *5*, 1195–1198.

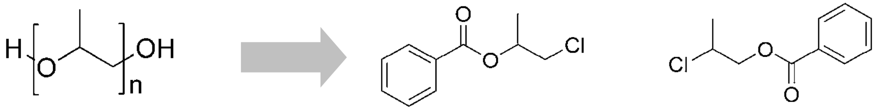
Depolymerization of Polyethers





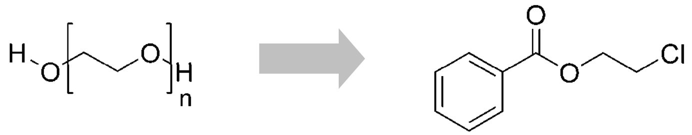
Polyethylene glycol
(M$_n$ ~100.000 g/mol)

Yield: 89%



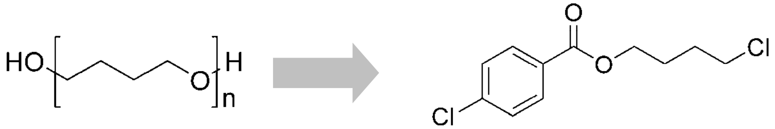
Polypropylene oxide
(M$_n$ ~2500 g/mol)

Yield: 68%



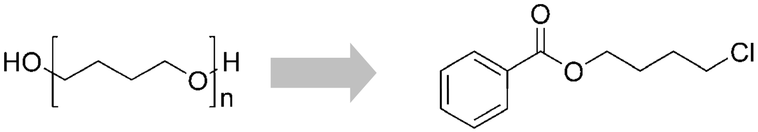
Polyethylene glycol
(M$_n$ ~1.000.000 g/mol)

Yield: 95%



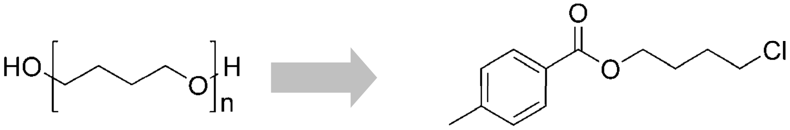
Polytetrahydrofuran
(M$_n$ ~1000 g/mol)

Yield: 92%



Polytetrahydrofuran
(M$_n$ ~1000 g/mol)

Yield: 83%

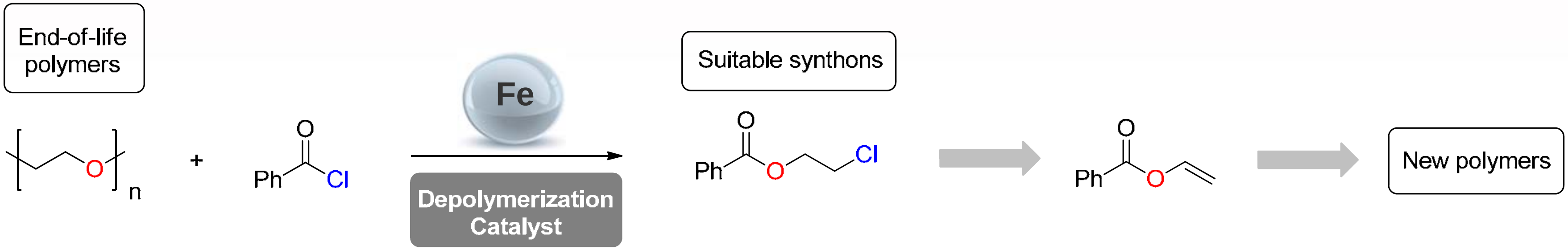


Polytetrahydrofuran
(M$_n$ ~1000 g/mol)

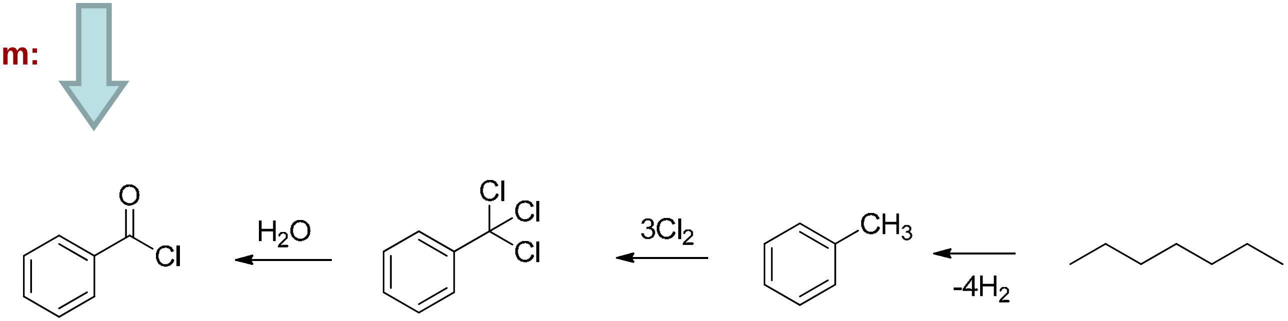
Yield: 89%

- S. Enthaler, M. Weidauer, *ChemSusChem* **2012**, *5*, 1195–1198.

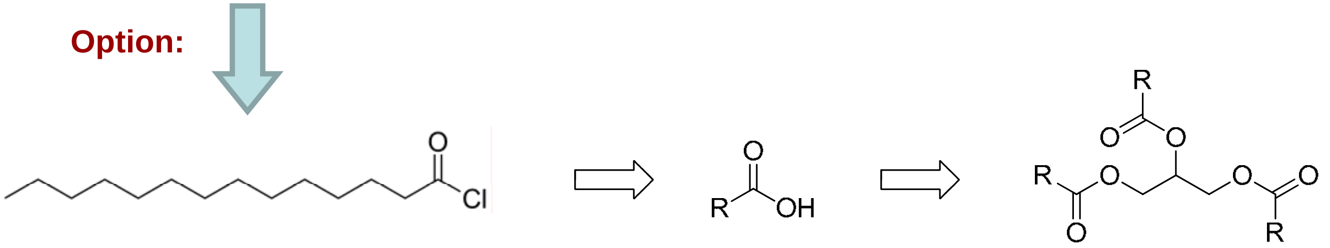
Depolymerization of Polyethers



Problem:



Option:

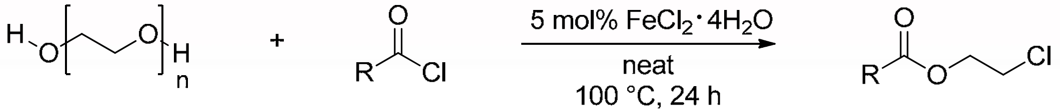


Renewable resources

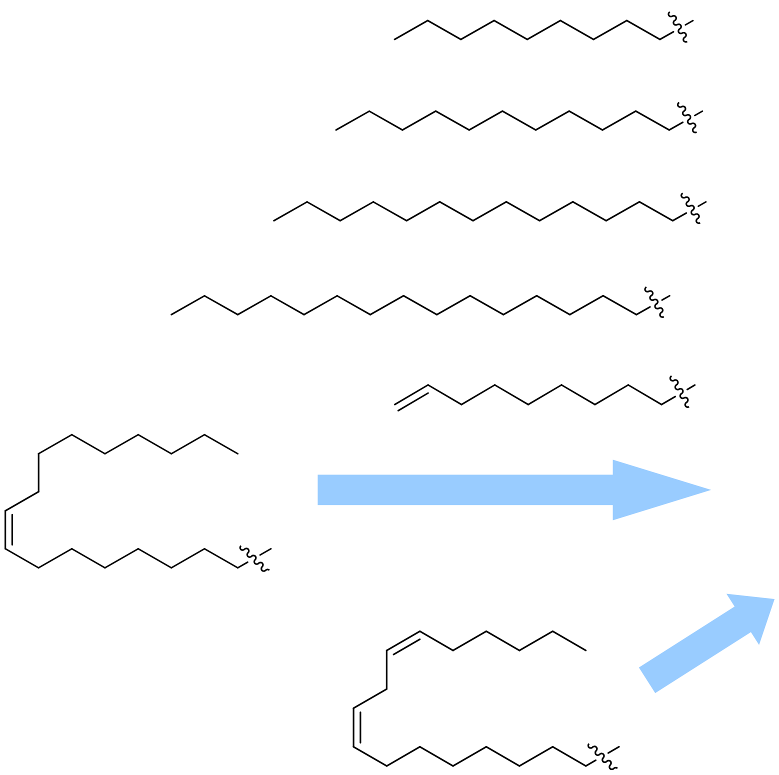
- **fatty acid chlorides**

- S. Enthaler, *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 239–245.

Depolymerization of Polyethers



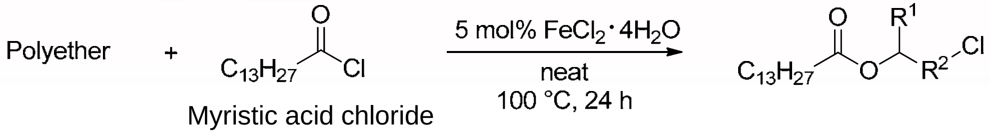
1 (M_n~300 g/mol) **2** **3**

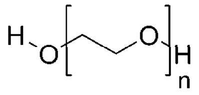


Entry	Substrate (C:D)[a]	Yield (3) [%]
1	capric acid chloride (10:0)	78
2	lauroyl chloride (12:0)	77
3	myristoyl chloride (14:0)	82
4	palmitoyl chloride (16:0)	75
5	10-undecenoyl chloride (11:1)	<1
6	oleic acid chloride (18:1)	39
7	linoleic acid chloride (18:2)	<1

[a] C:D = number of carbons: number of double bonds.

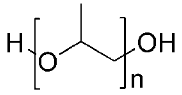
Depolymerization of Polyethers





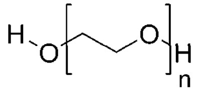
Polyethylene glycol
(M_n ~1.000 g/mol)

Yield: 69 %



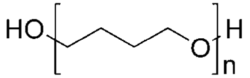
Polypropylene oxide
(M_n ~2500 g/mol)

Yield: 77 %



Polyethylene glycol
(M_n ~1.000.000 g/mol)

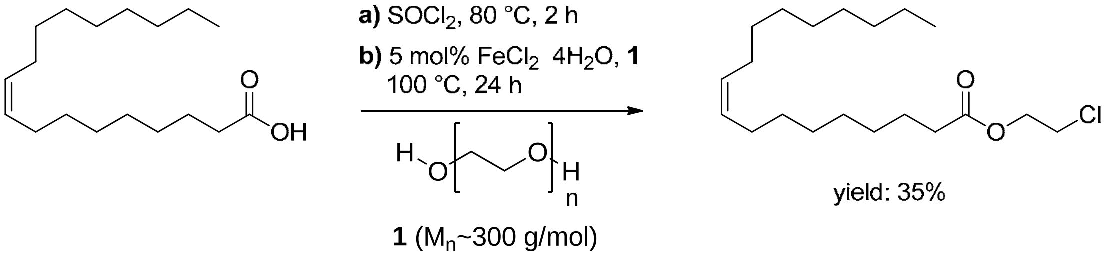
Yield: 56 %



Polytetrahydrofuran
(M_n ~1000 g/mol)

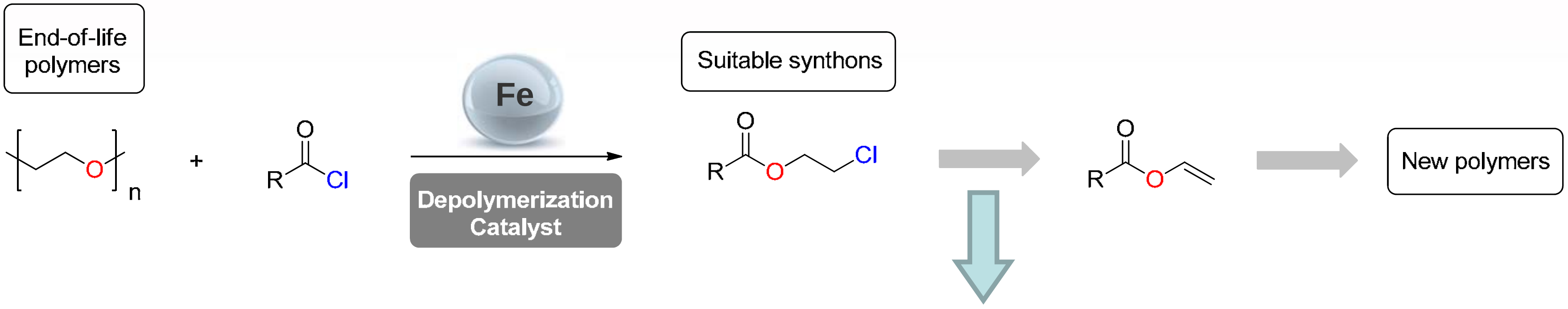
Yield: 57 %

- ***in situ* generation of the acid chloride**



- S. Enthaler, *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 239–245.

Depolymerization of Polyethers



End-of-life polymers

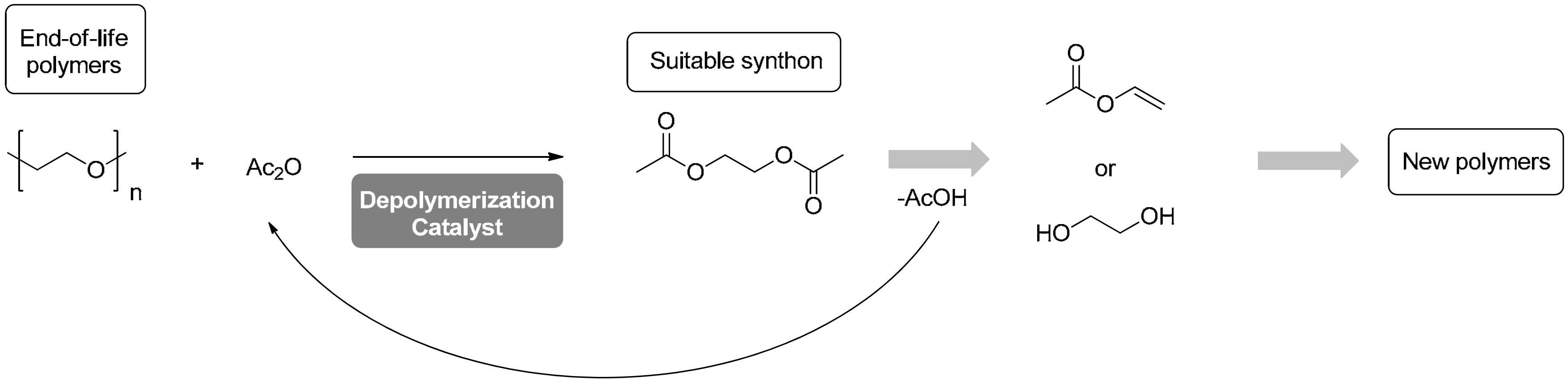
Suitable synthons

Depolymerization Catalyst

New polymers

Problem: HCl formation

Option:



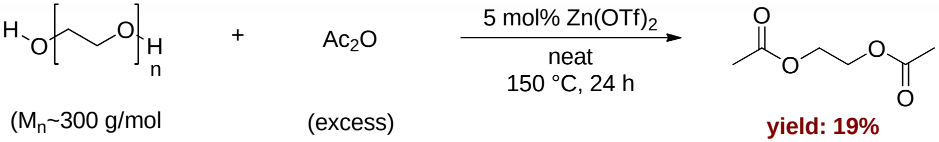
End-of-life polymers

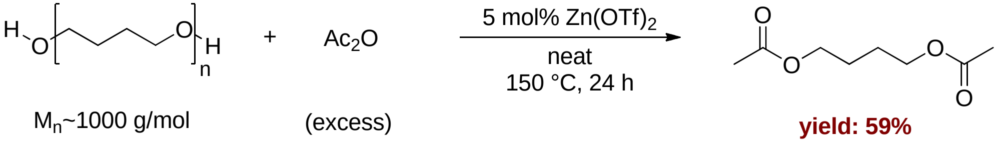
Suitable synthon

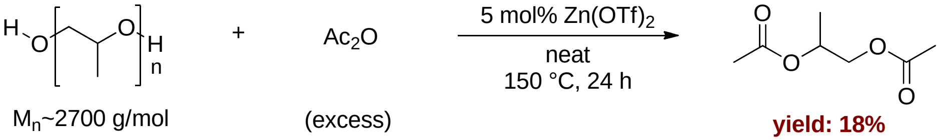
Depolymerization Catalyst

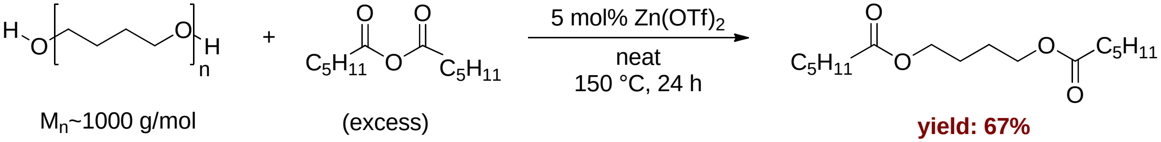
New polymers

Depolymerization of Polyethers



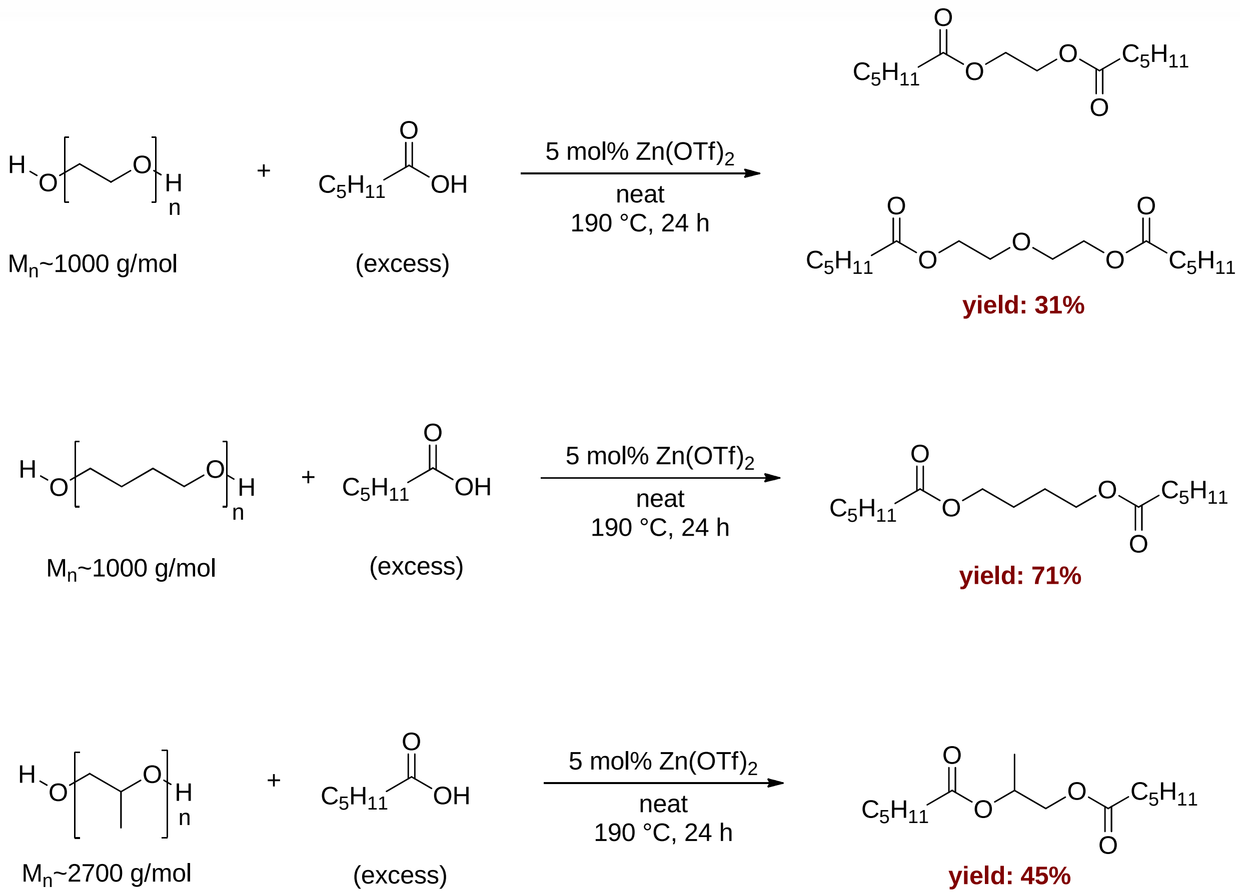






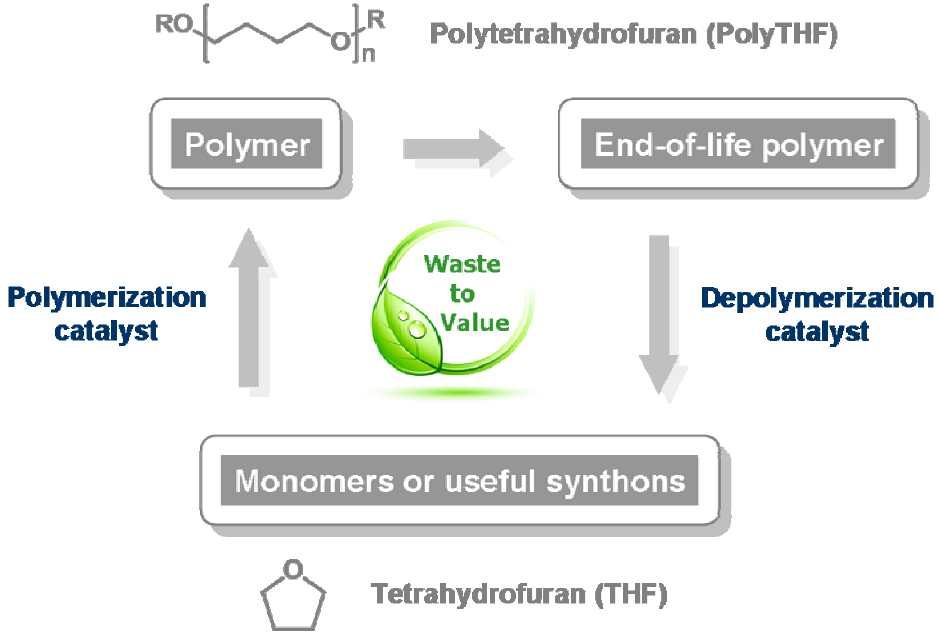
- S. Enthaler, **2014**, *submitted*.

Depolymerization of Polyethers



- S. Enthaler, **2014**, *submitted*.

Depolymerization of Polyethers



Polytetrahydrofuran (PolyTHF)

Polymer

End-of-life polymer

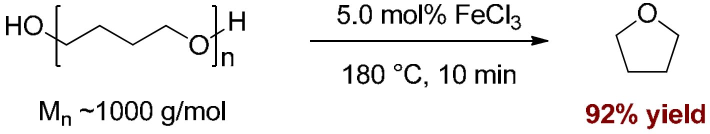
Polymerization catalyst

Waste to Value

Depolymerization catalyst

Monomers or useful synthons

Tetrahydrofuran (THF)

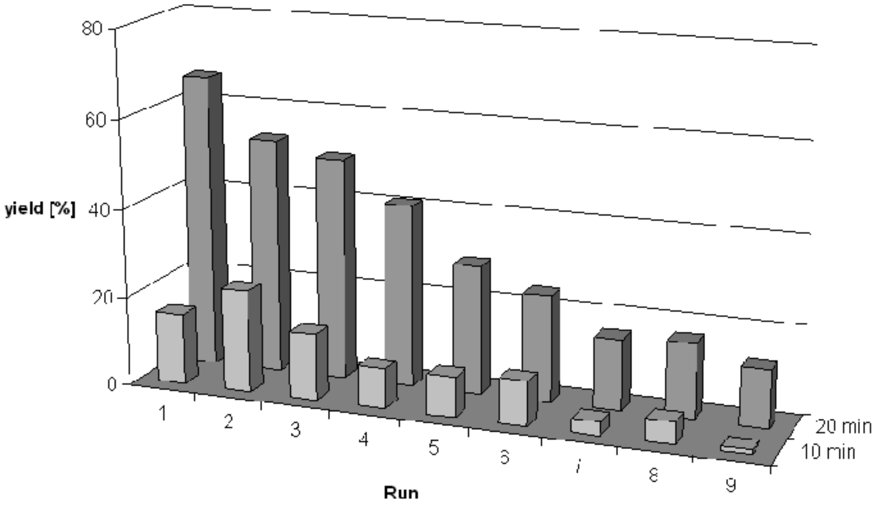


5.0 mol% $FeCl_3$

180 °C, 10 min

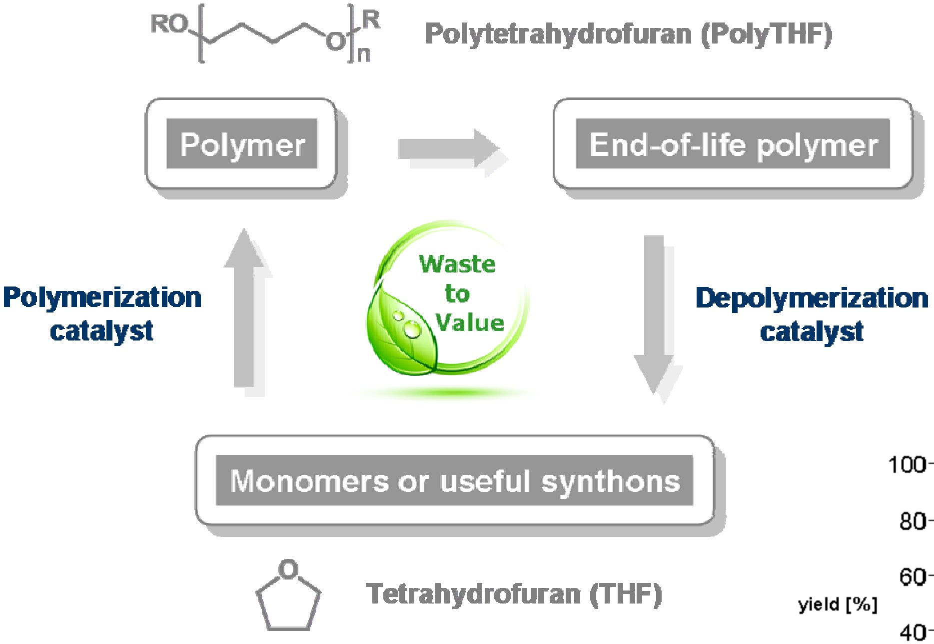
M_n ~1000 g/mol

92% yield



- S. Enthaler, A. Trautner, *ChemSusChem* **2013**, *6*, 1334–1336.

Depolymerization of Polyethers



Polytetrahydrofuran (PolyTHF)

Polymer

End-of-life polymer

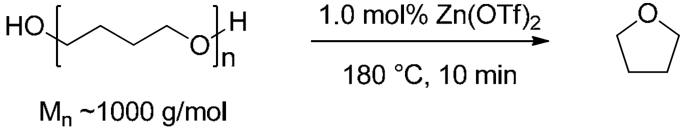
Polymerization catalyst

Waste to Value

Depolymerization catalyst

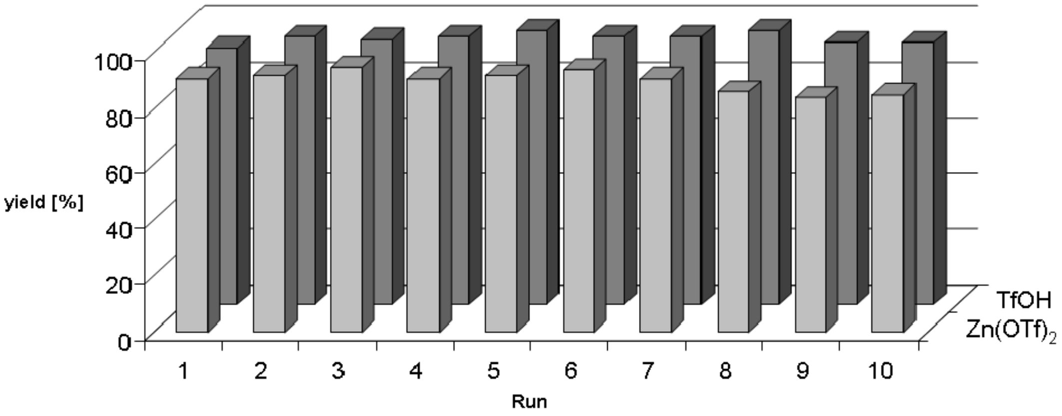
Monomers or useful synthons

Tetrahydrofuran (THF)



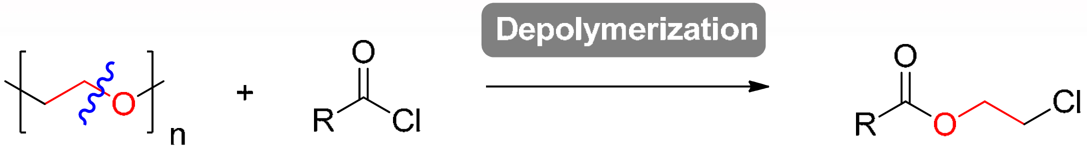
M_n ~1000 g/mol

TON = 900
TOF = 180 h^{-1}



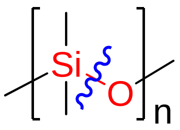
- S. Enthaler, *J. Appl. Poly. Sci.* **2014**, *DOI: 10.1002/app.39791*.

Depolymerization of Silicones

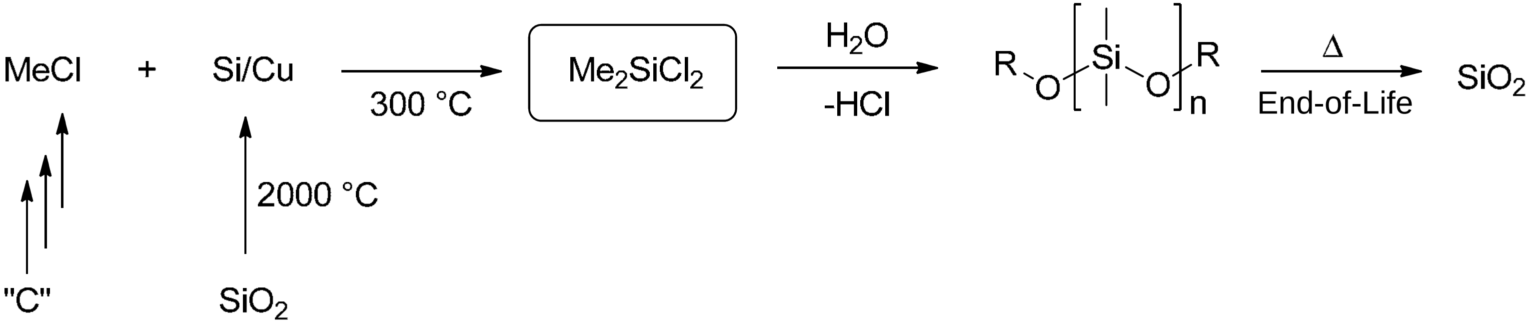


New polymers

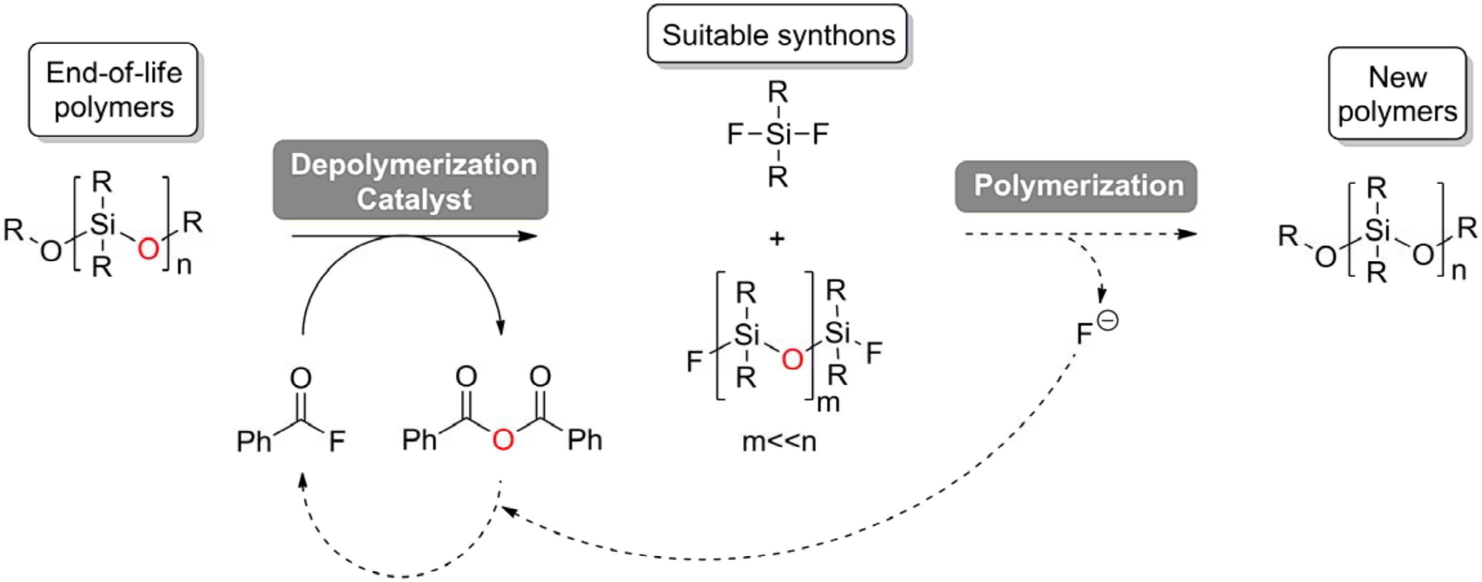
Transfer of the concept to polysiloxanes?



- **Polysiloxane synthesis**

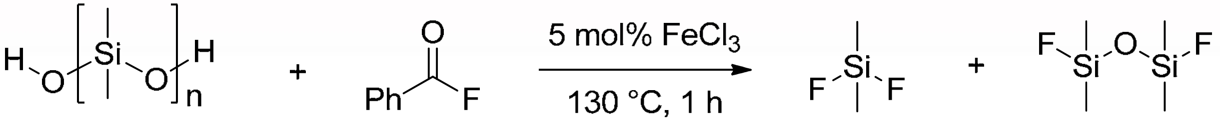


Depolymerization of Silicones



- S. Enthaler, *Angew. Chem. Int. Ed.* **2014**, *DOI:* 10.1002/anie.201309299.

Depolymerization of Silicones



1 M_n ~550 g/mol

2 (2 equiv.)

3

4

64% yield

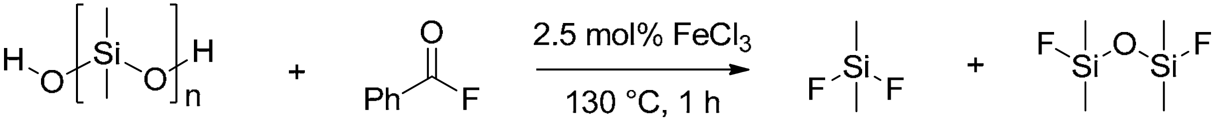
16% yield

80% yield

bp: ~3 °C

bp: ~70 °C

Optimization study



1 M_n ~550 g/mol

2 (2.5 equiv.)

3

4

62% yield

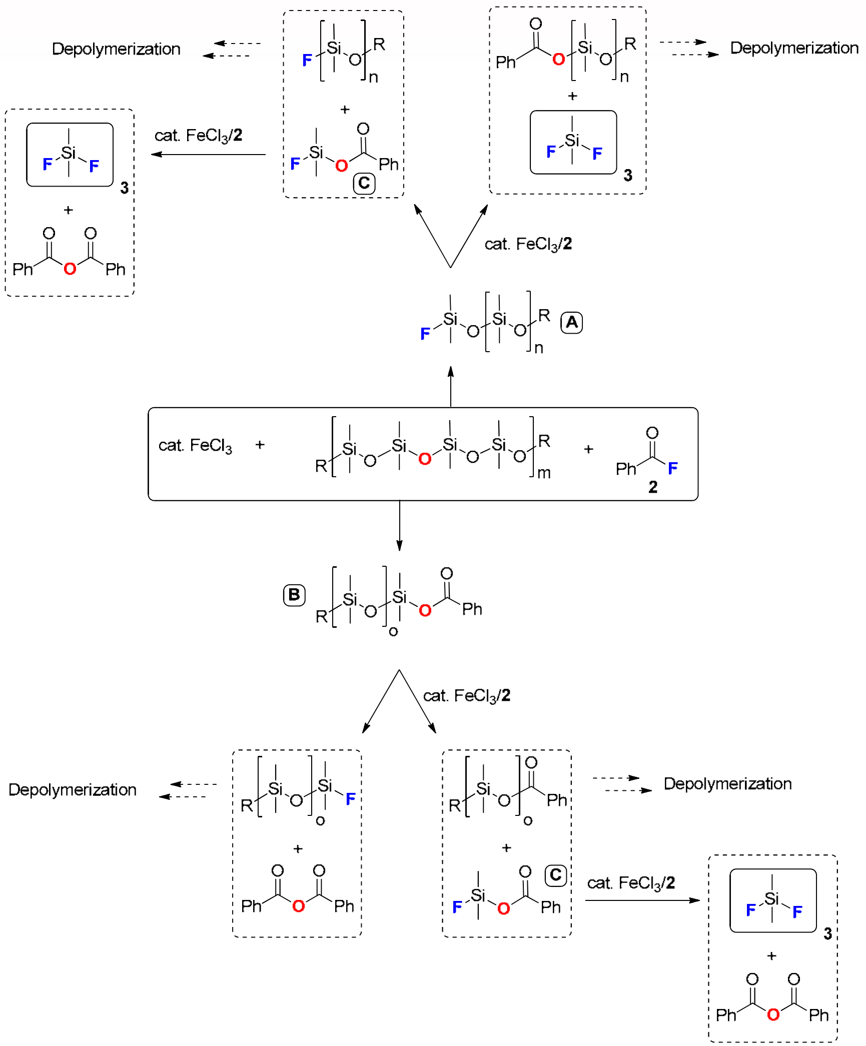
28% yield

90% yield

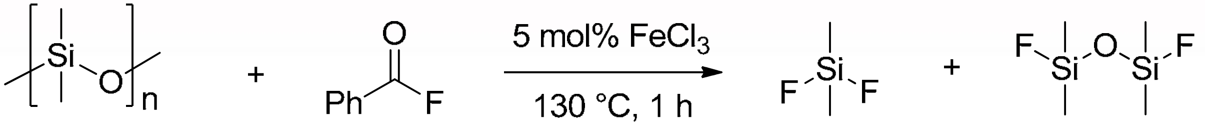
Reaction set-up

- S. Enthaler, R. Kretschmer, **2014**, *submitted*.

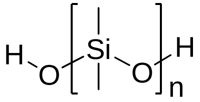
Depolymerization of Silicones



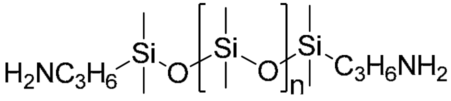
Depolymerization of Silicones



2 **3** **4**

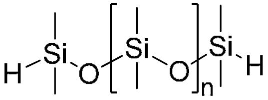


88% yield (69/19)
(M_n ~110.000 g/mol)

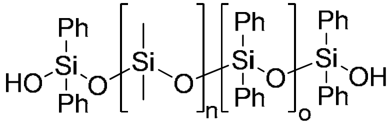


56% yield (47/9)
(M_n ~2.500 g/mol)

95% yield (72/23)
(M_n ~5.600 g/mol)



65% yield (49/16)
(M_n ~580 g/mol)



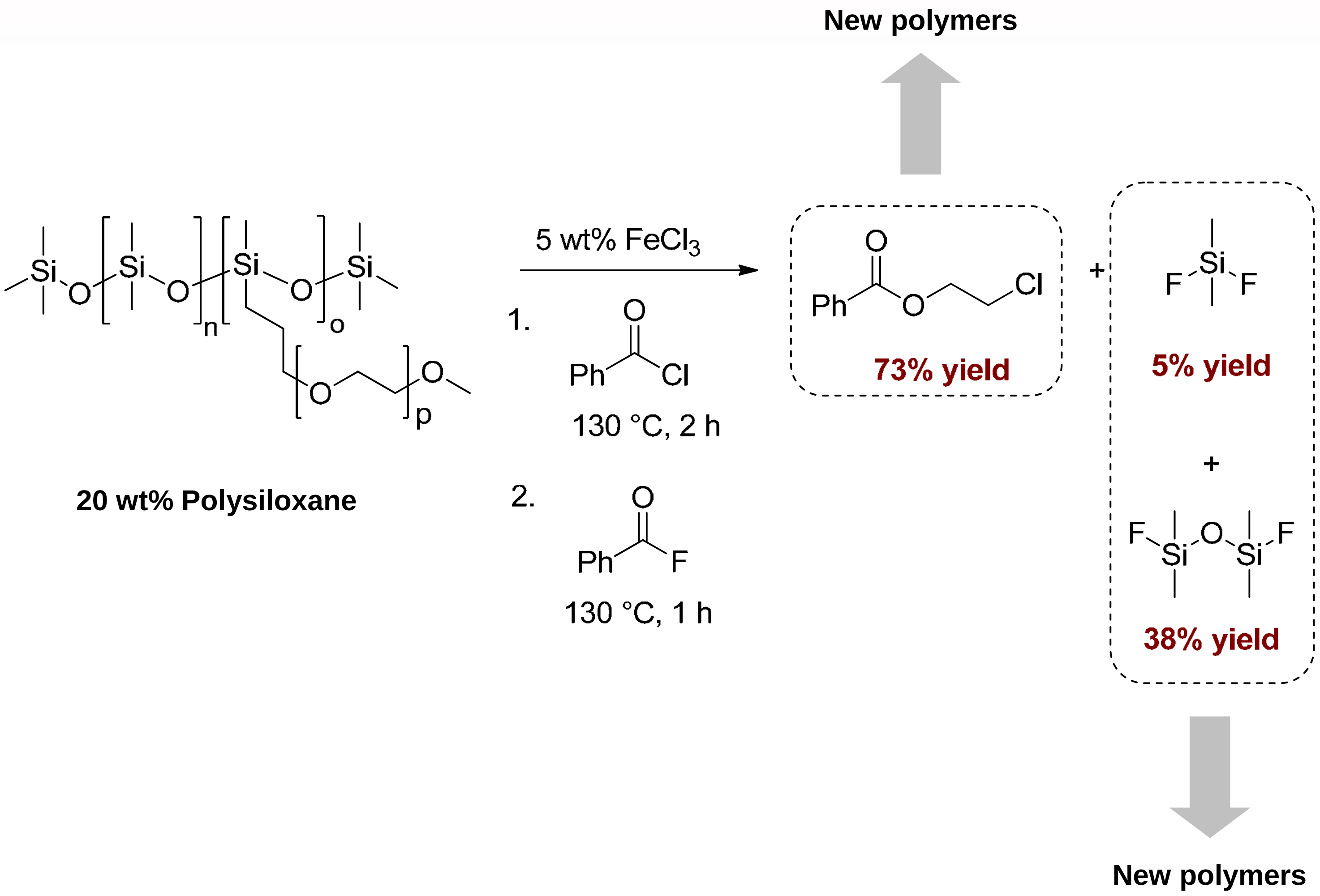
60% yield (40/10)[a)]
(M_n ~580 g/mol)
87% yield (Ph_2SiF_2)

Silicone oil
(viscosity 30.000 cSt)

81% yield (74/7)

a) 95:5 mole ratio of dimethylsiloxane:diphenylsiloxane

Depolymerization of Silicones



New polymers

20 wt% Polysiloxane

5 wt% $FeCl_3$

1. PhCOCl, 130 °C, 2 h

2. PhCOF, 130 °C, 1 h

73% yield

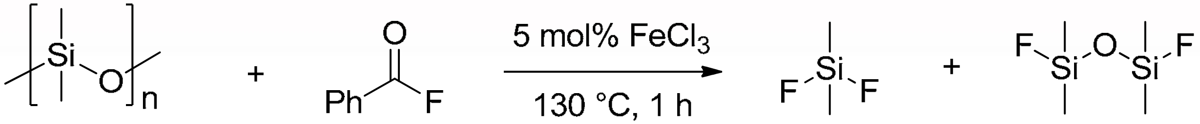
5% yield

38% yield

New polymers

- S. Enthaler, M. Weidauer, *ChemSusChem* **2012**, *5*, 1195–1198.

Depolymerization of Silicones



1 g

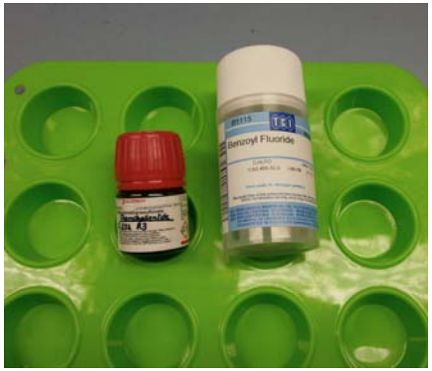
2

3

0.4 g

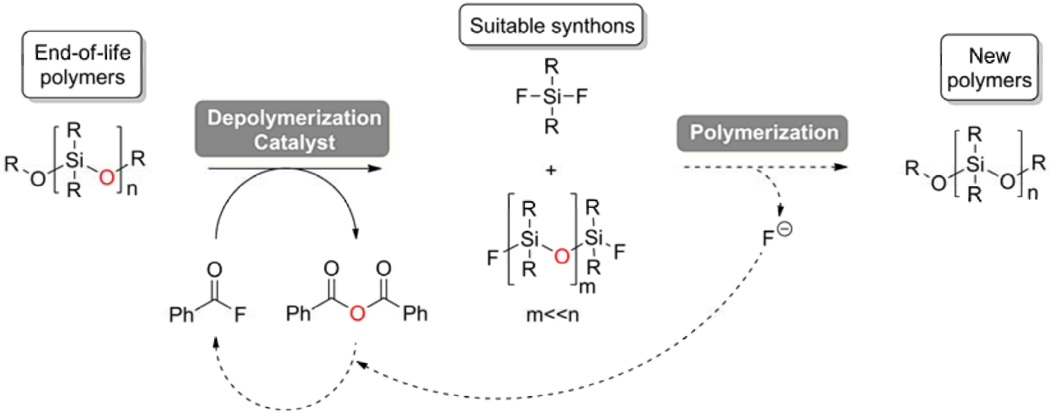
4

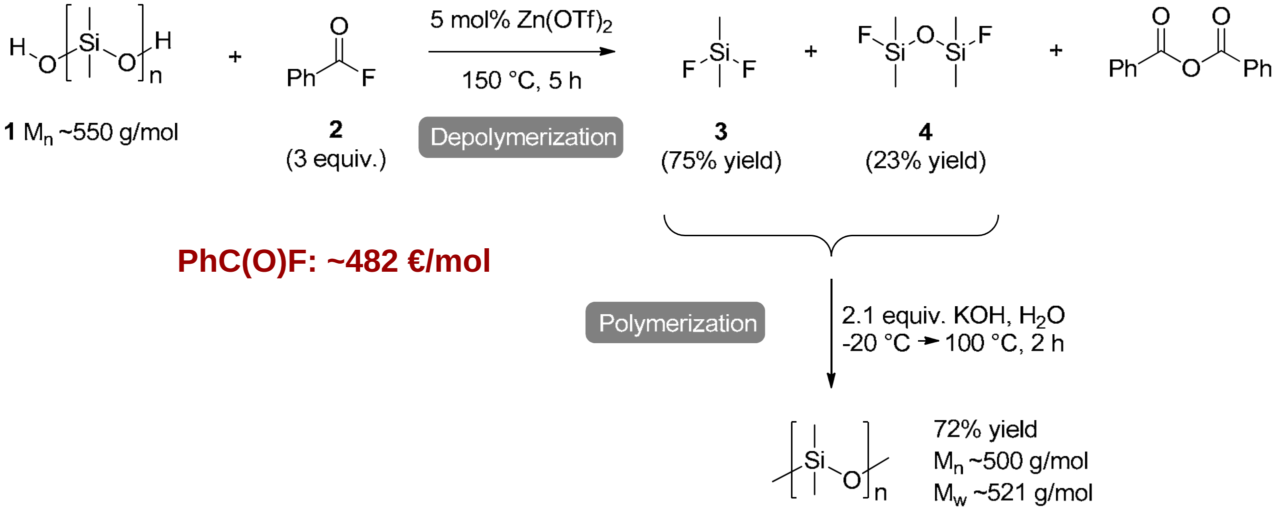
0.3 g



Silicone baking cup

Depolymerization of Silicones

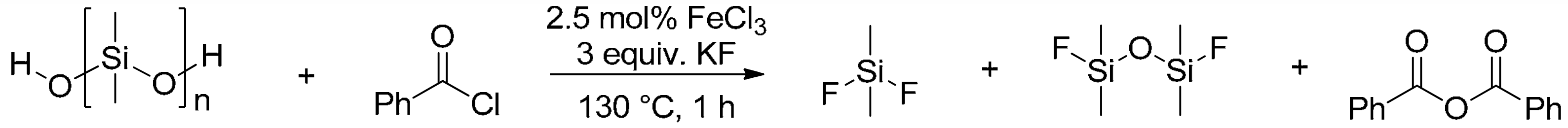




PhC(O)F: ~482 €/mol

- S. Enthaler, *Angew. Chem. Int. Ed.* **2014**, *DOI:* 10.1002/anie.201309299.

Depolymerization of Silicones



1 M_n ~550 g/mol

(3 equiv.)

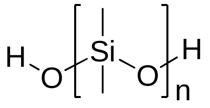
3

51% yield

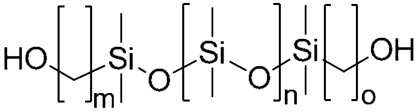
4

17% yield

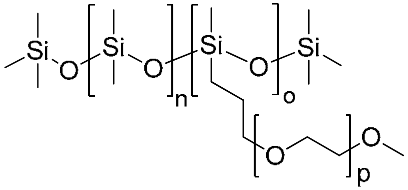
PhC(O)Cl/KF: ~22 €/mol
PhC(O)F: ~482 €/mol



47% yield
(M_n ~110.000 g/mol)



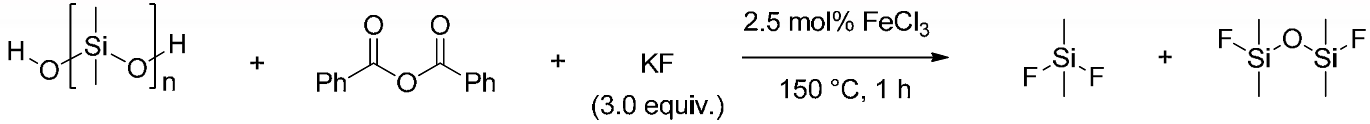
35% yield
(M_n ~5.600 g/mol)



65% yield
(20 wt% Polysiloxane)

- S. Enthaler, R. Kretschmer, **2014**, *submitted*.

Depolymerization of Silicones

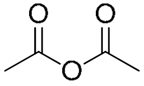


1 M_n ~550 g/mol

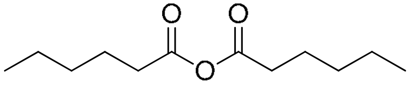
(1.5 equiv.)

3
(74% yield)

4
(4% yield)

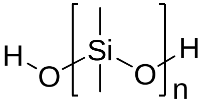


3: 36% yield
4: 4% yield

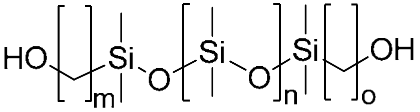


3: 78% yield
4: 1% yield

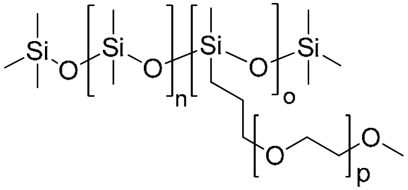
PhC(O)O(O)CPh/KF: ~46 €/mol
PhC(O)Cl/KF: ~22 €/mol
PhC(O)F: ~482 €/mol



60% yield
(M_n ~110.000 g/mol)



48% yield
(M_n ~5.600 g/mol)

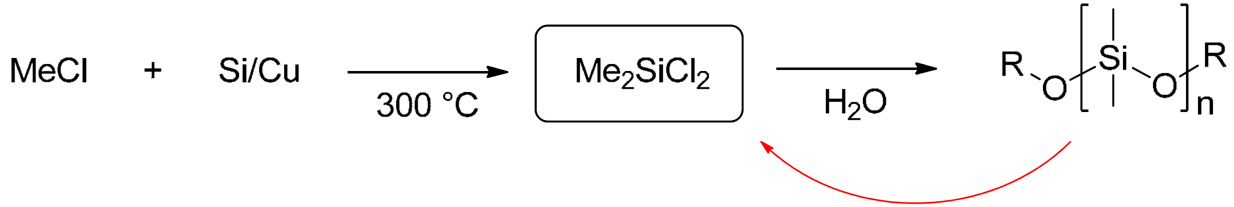


71% yield
(20 wt% Polysiloxane)

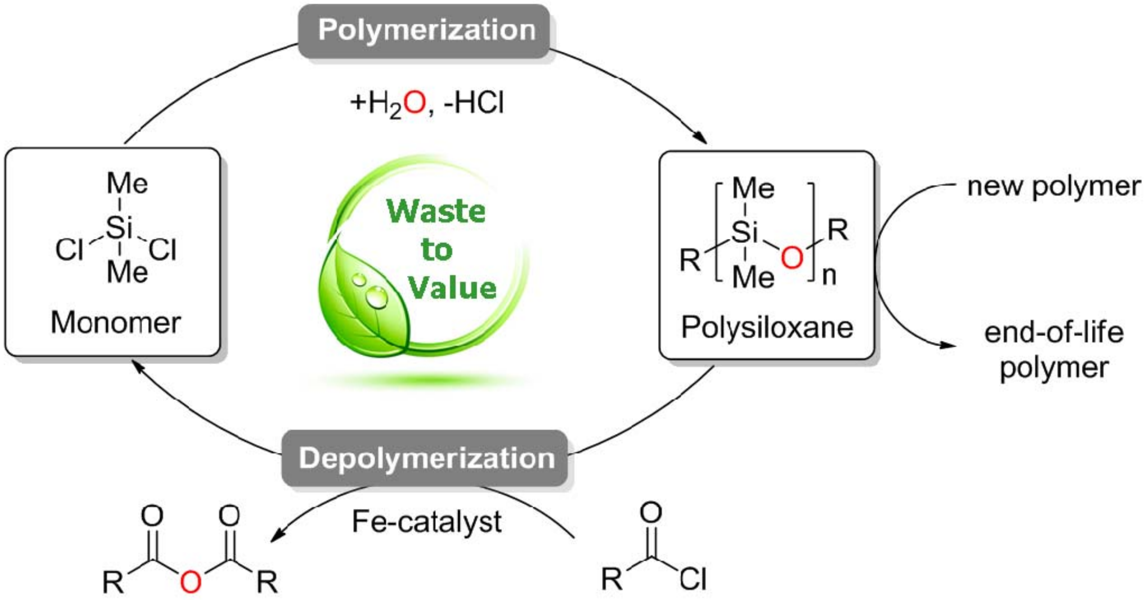
- S. Enthaler, R. Kretschmer, **2014**, *submitted*.

Depolymerization of Silicones

- **Silicone Synthesis:**

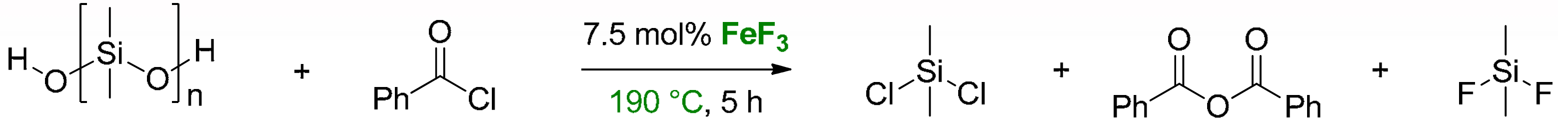


- **Silicone Recycling:**



- B. A. Ashby, GB 990657, **1965**.
- S. N. Borisov, M. G. Voronkov, N. G. Sviridova, *Zh. Obshch. Khim.* **1969**, *39*, 559-564.

Depolymerization of Silicones



1 M_n ~550 g/mol

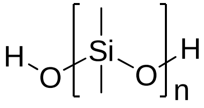
2 (3 equiv.)

3

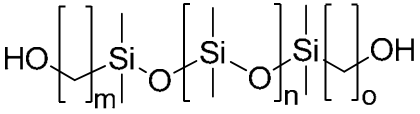
86% yield

traces

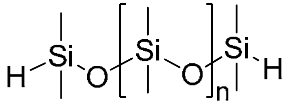
(**$FeCl_3$:** 32% yield)



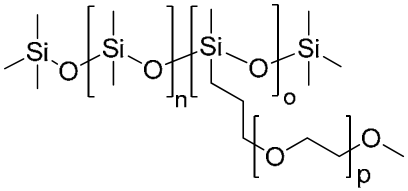
82% yield
(M_n ~110.000 g/mol)



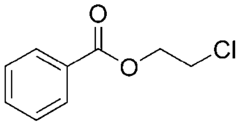
40% yield
(M_n ~5.600 g/mol)



45% yield
(M_n ~580 g/mol)



35% yield

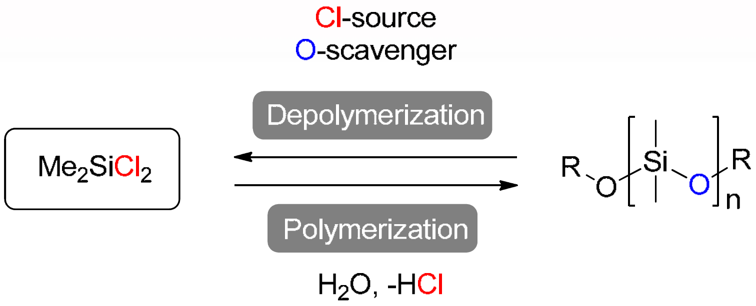


91% yield

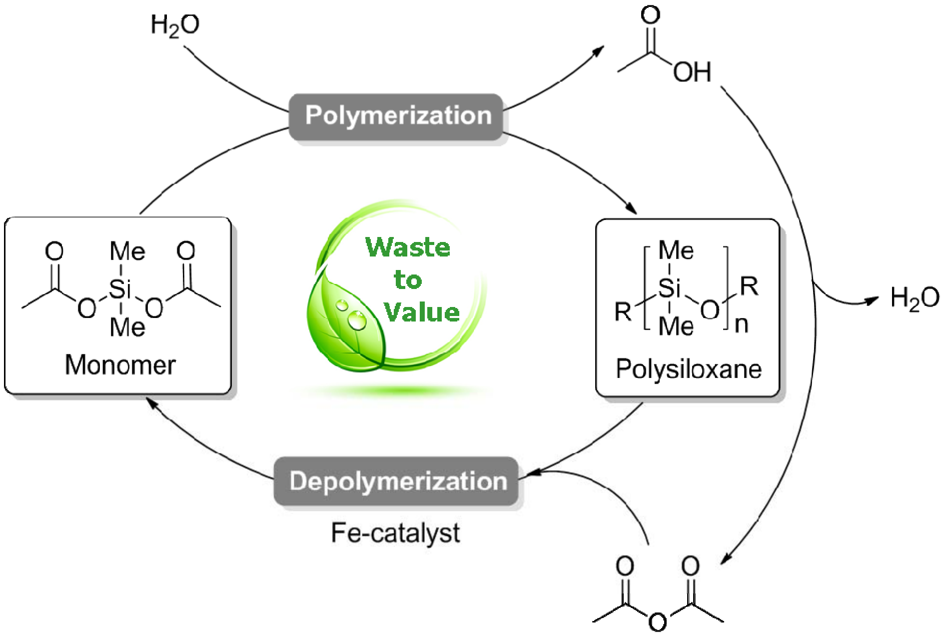
- S. Enthaler, **2014**, *submitted*.

Depolymerization of Silicones

- **Polymerization/Depolymerization:**



- **Silicone Recycling / Depolymerization / Reagent Recycling:**

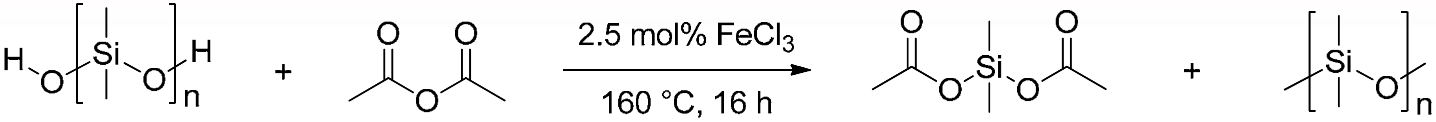


Ac_2O: ~3 €/mol
PhC(O)Cl/KF: ~22 €/mol
PhC(O)O(O)CPh/KF: ~46 €/mol
PhC(O)F: ~482 €/mol

- S. N. Borisov, M. G. Voronkov, N. G. Sviridova, *Zh. Obshch. Khim.* **1969**, *39*, 559-564.

Depolymerization of Silicones

- **Depolymerization:**

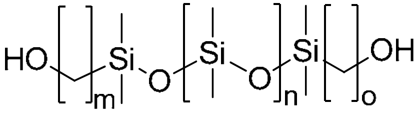


M_n~ 550 g/mol

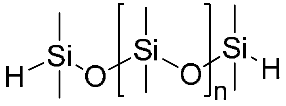
2 equiv.

51% yield

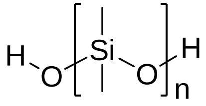
e.g. n = 4



37% yield
(M_n ~5.600 g/mol)

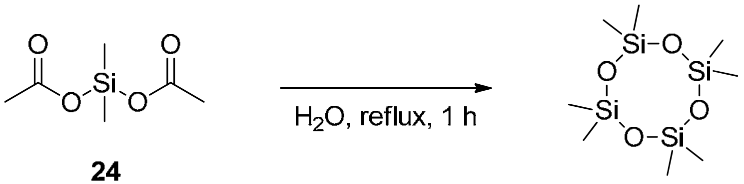


35% yield
(M_n ~580 g/mol)



29% yield
(M_n ~110.000 g/mol)
$FeCl_2$ $4H_2O$

- **Polymerization:**



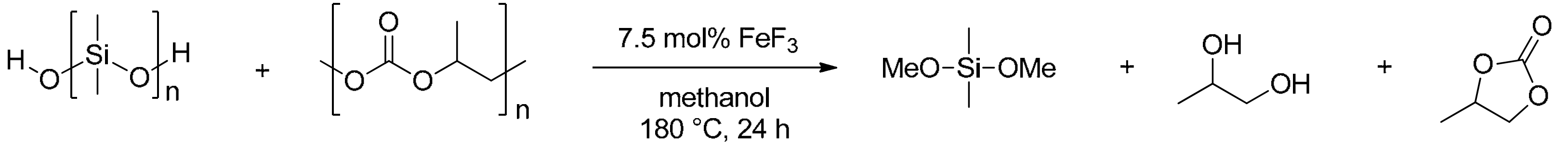
+ minor products

24

25 (yield: 55%)

- S. Enthaler, *submitted*.

Depolymerization of Silicones



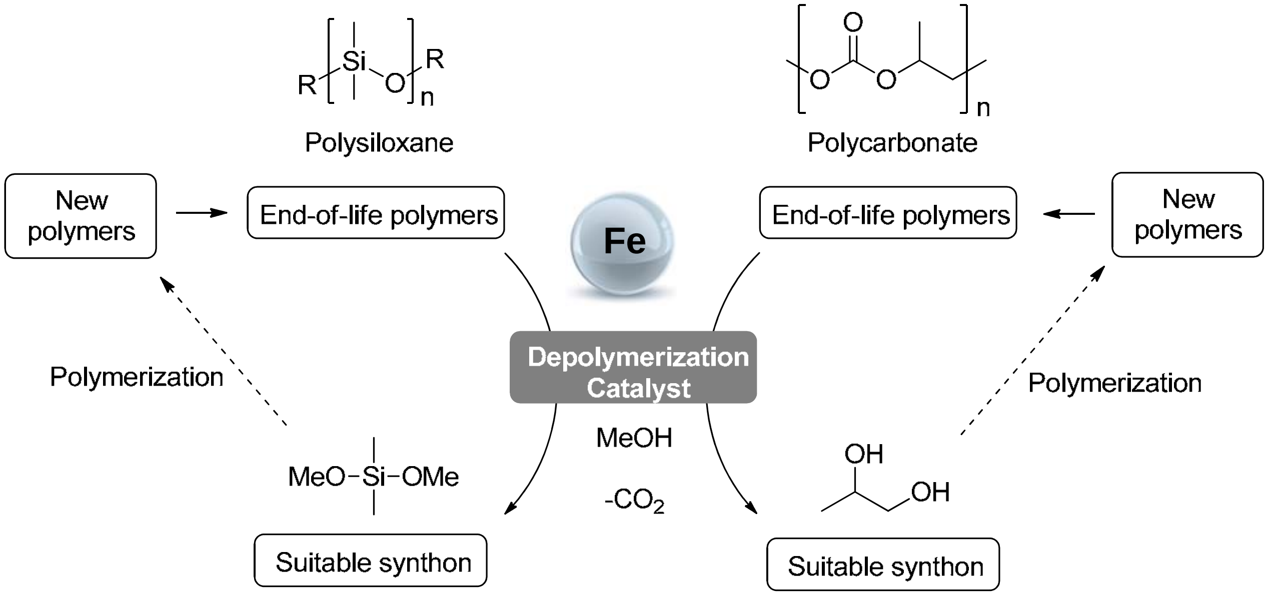
1 M_n~550 g/mol

2 M_n~50000 g/mol

3 **18% yield**

4 **14% yield**

5 **32% yield**



Polysiloxane

Polycarbonate

New polymers

End-of-life polymers

Fe

Depolymerization Catalyst

MeOH

$-CO_2$

Polymerization

Suitable synthon

End-of-life polymers

New polymers

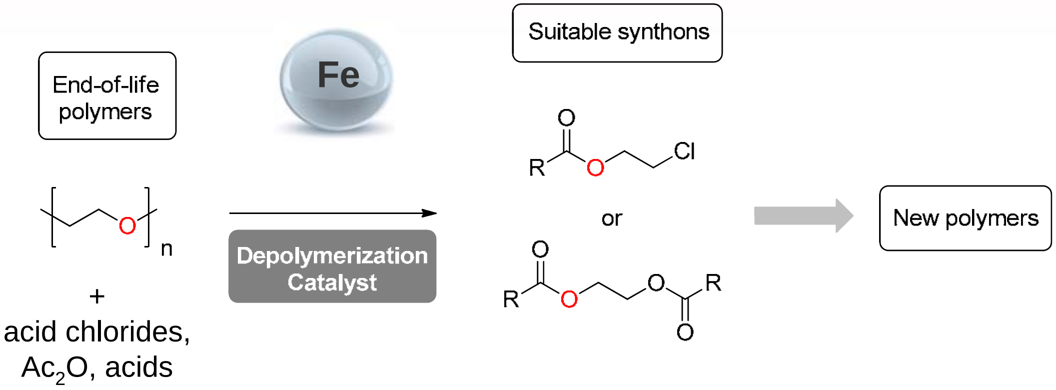
Polymerization

Suitable synthon

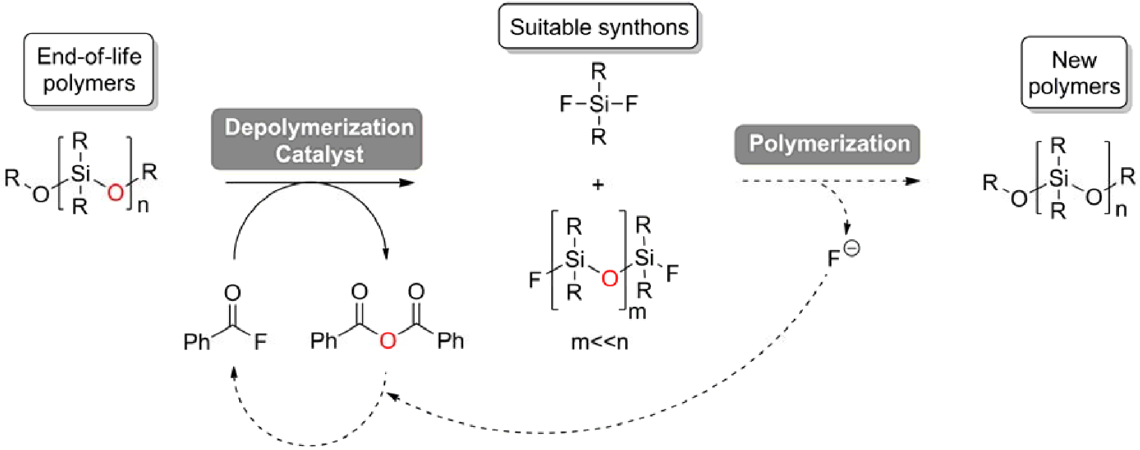
- a) M. Okamoto, S. Suzuki, E. Suzuki, *Appl. Catal. A: General* **2004**, *261*, 239-245
- b) M. Okamoto, K. Miyazaki, A. Kado, S. Suzuki, E. Suzuki, *Catal. Lett.* **2003**, *88*, 115-118

Summary

- **Depolymerization of Polyethers**



- **Depolymerization of Polysiloxanes**



Acknowledgments

- **Dr. Chika Inoue Someya**
- **Dr. Michael Haberberger**
- **Maik Weidauer**
- **Peter Döhlert**
- **Frank Czerny**
- **Heidi Trutwin**

- **Prof. Shigeyoshi Inoue (TUB)**
- **Dr. Elisabeth Irran (TUB)**
- **Dr. Jan Dirk Epping (TUB)**
- **Dr. Robert Kretschmer**

(University of California San Diego)

Waste a “renewable“ resource for the future?

Thank you for your attention!