The role of mother earth, water, air and fire in the development of new polymer materials

Cor Koning

DPI Annual meeting
Maastricht, November 21, 2007

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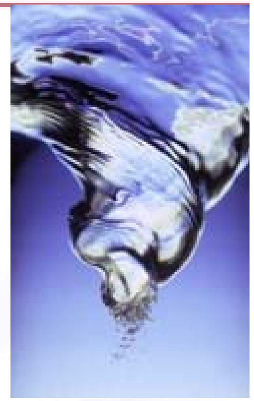
The role of mother earth, water, air and fire in the development of new polymer materials

or



'The elements' and materials development

Four examples

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Novel bio-based polyesters: Synthesis, characterization and evaluation

TA Coating Technology, DPI project # 451

B.A.J. Noordover[1], R. Duchateau[1], C.E. Koning[1], R.A.T.M. van Benthem[2], Andreas Heise[1], R. Koelewijn[3], J. van Haveren[3] and D.S. van Es[3]

[1] Laboratory of Polymer Chemistry, Eindhoven University of Technology, The Netherlands
[2] Laboratory of Materials and Interface Chemistry, Eindhoven University of Technology
[3] Agrotechnology and Food Innovations, Wageningen University and Research Centre

Renewable thermoset powder coatings

- **<u>general characteristics</u>**

- solvent-free coating systems
- mixing of components (i.e. resin, cross-linker and additives) by extrusion
- powder applied to substrate using electrostatic interactions
- subsequent thermally induced flow and curing

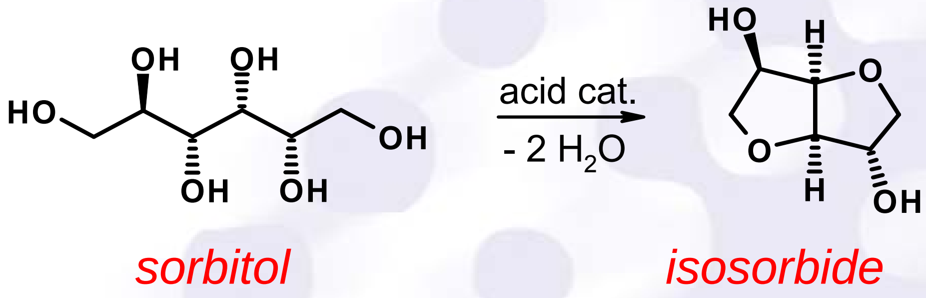
- **<u>resin requirements</u>**

- storage stability and mechanical performance: $T_g > 45$ ºC already for moderate M_n, 2000 – 6000 g/mol
- functionality $f \geq 2$ (often: carboxylic acid or hydroxyl functionalities)
- amorphous and colorless
- appropriate flow properties at T_{cure}
- UV stability → aliphatic rather than aromatic polyesters

Why use renewables?

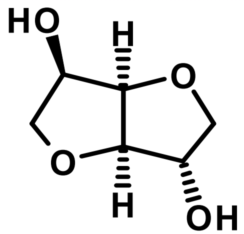
- building blocks with high functionality available from nature, suitable for polymer network formation
- decreasing fossil feedstock (and increasing oil prices)
- rigid, high Tg providing aliphatic monomers readily available
  for example: *dianhydrohexitols*

- available feedstock: starch (corn, potatoes etc.), cellulose, vegetable oils etc. *'From corn to coatings'*

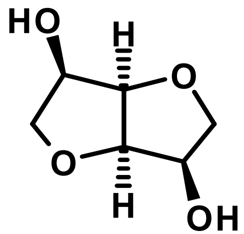


Synthesis of 1,4:3,6-dianhydro-D-sorbitol (isosorbide) from sorbitol

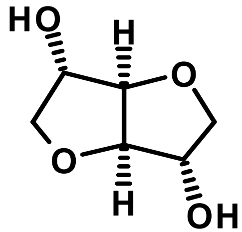
Monomers from biomass



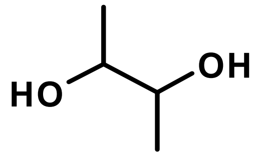
isosorbide
(IS)



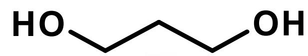
isomannide
(IM)



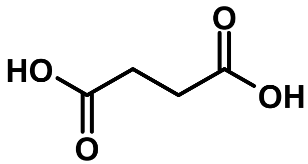
isoidide
(II)



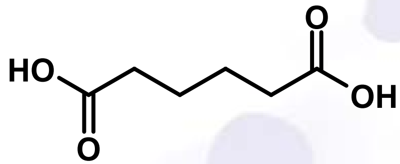
2,3-butanediol
(BD)



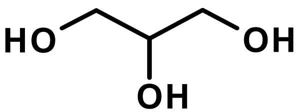
1,3-propanediol
PD)



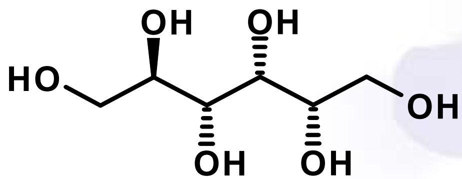
succinic acid
(SA)



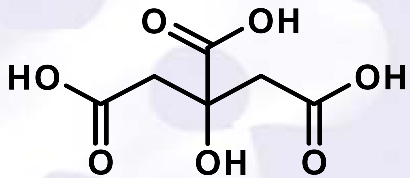
adipic acid
(AA)



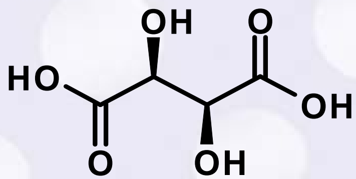
glycerol
(GLY)



sorbitol

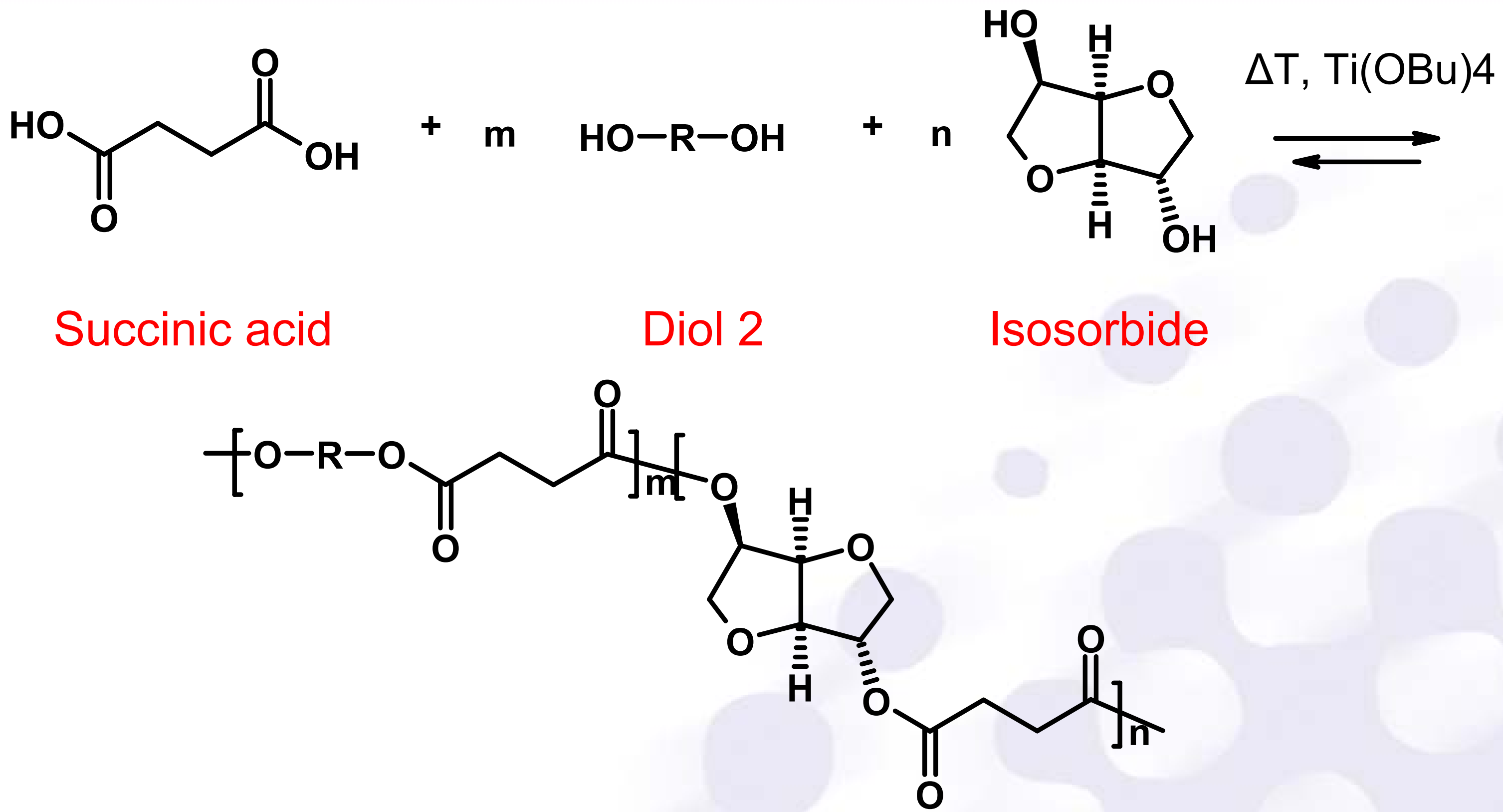


citric acid
(CA)



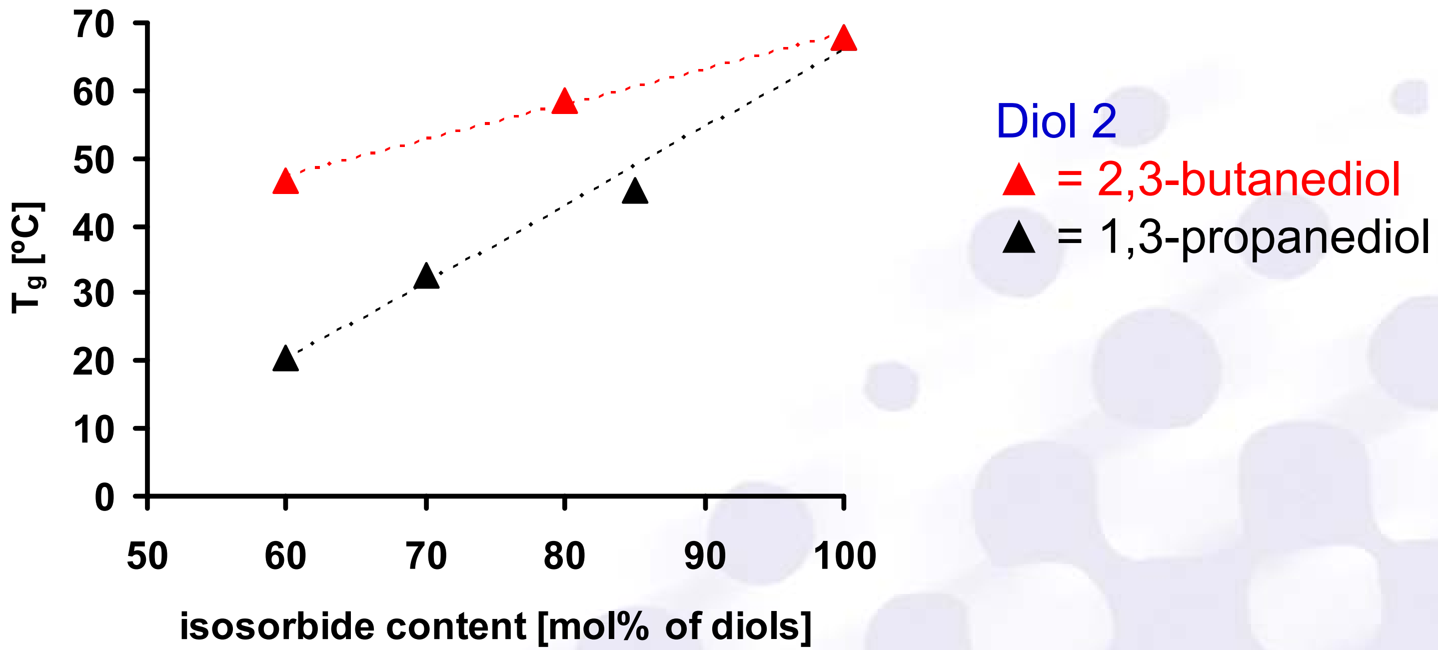
tartaric acid

Melt polycondensation



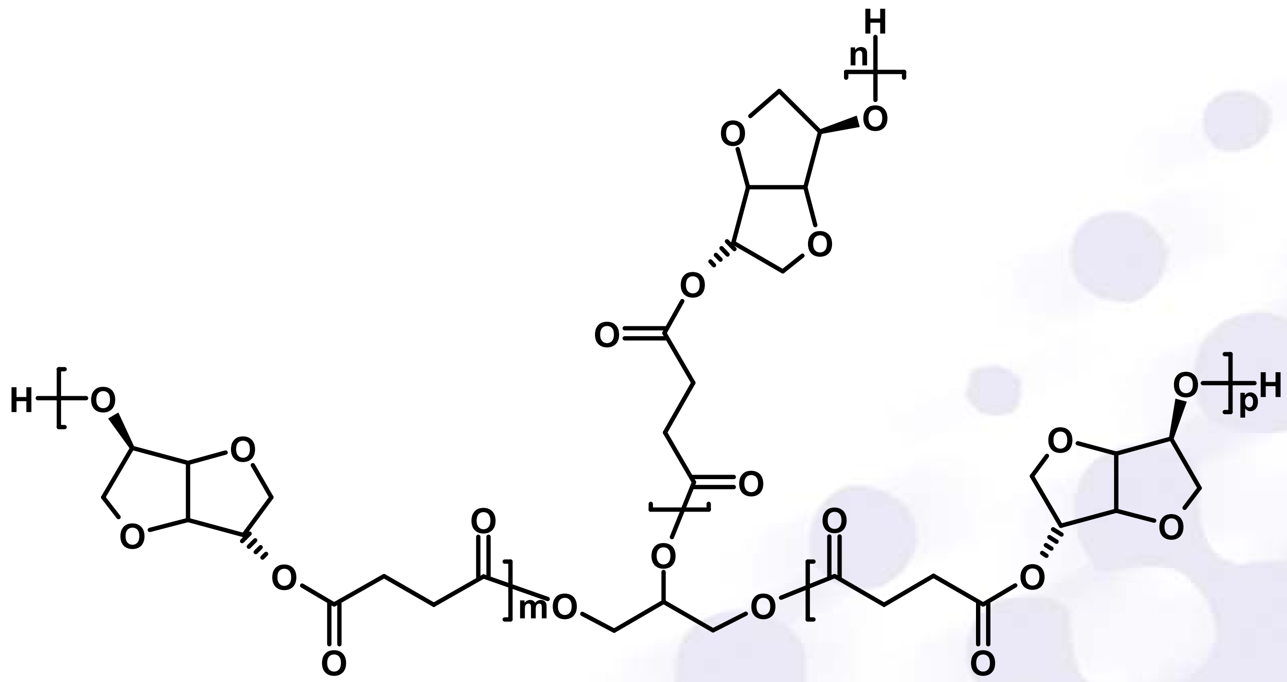
- polyesterification under inert gas flux, followed by vacuum processing
- typical temperatures: 180 – 230 ºC (not too long at 230 ºC !!!)
- typical pressures (2nd stage): 1-5 mbar

Succinic anhydride + Isosorbide + second diol



Molar mass can be controlled (2000-6000 g/mol

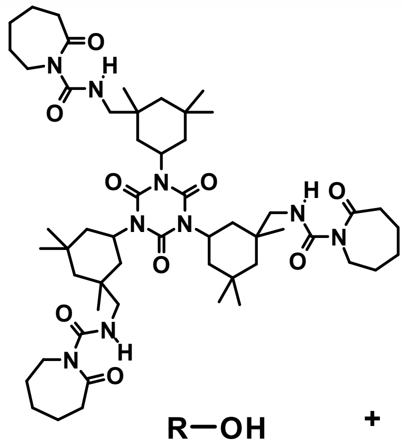
Enhancing OH functionality with glycerol



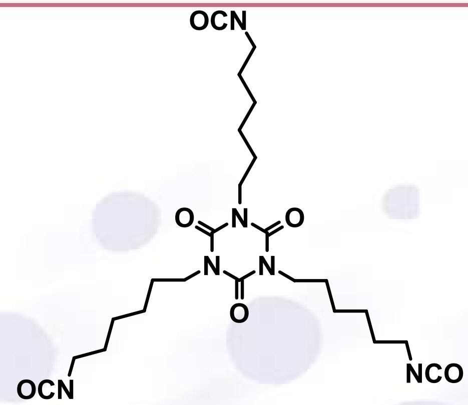
OH groups can easily be transformed into COOH groups by reaction with citric acid

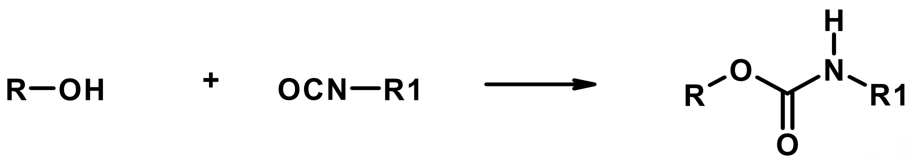
B.A.J. Noordover et al, Biomacromolecules, 2007

Curing with petrochemical-based curing agents

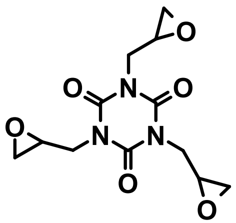


OH-functional

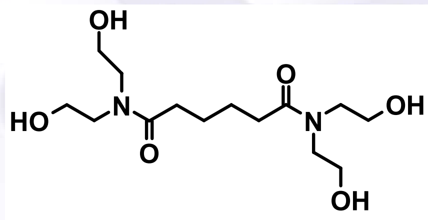


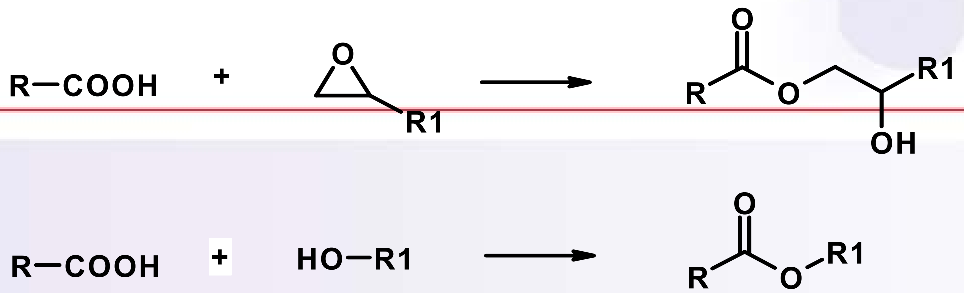


urethane



COOH-functional





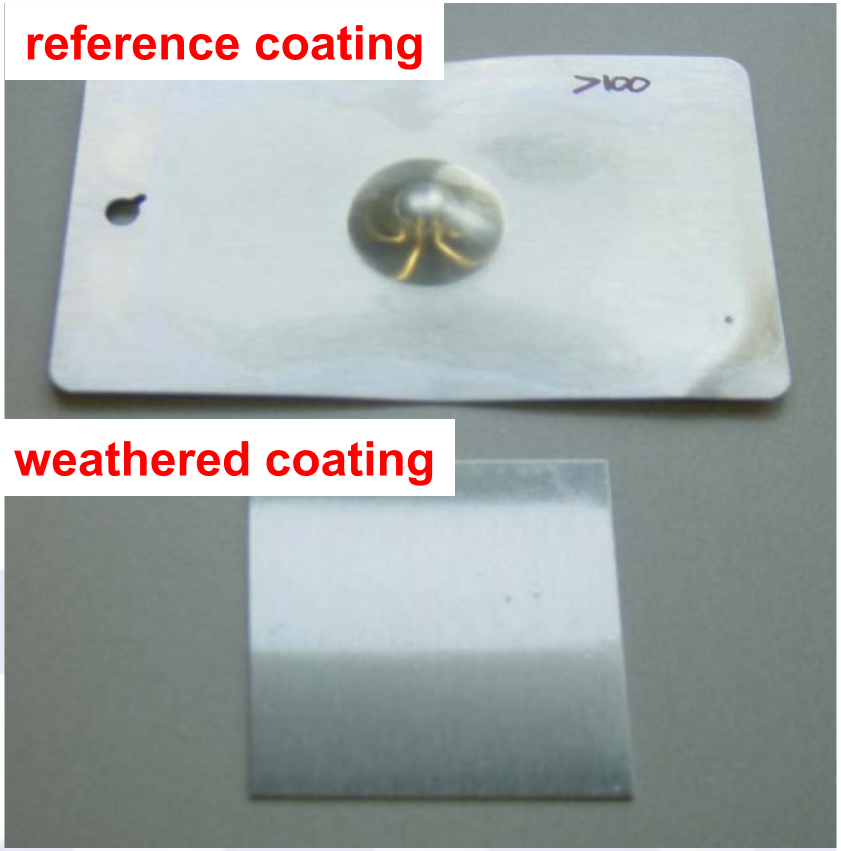
ester

Appearance, toughness and UV-stability

OH functional, cured with triisocyanate

COOH functional, cured with tri-epoxide

COOH functional, cured with Tetra-hydroxy



No yellowing under high intensity mercury lamp

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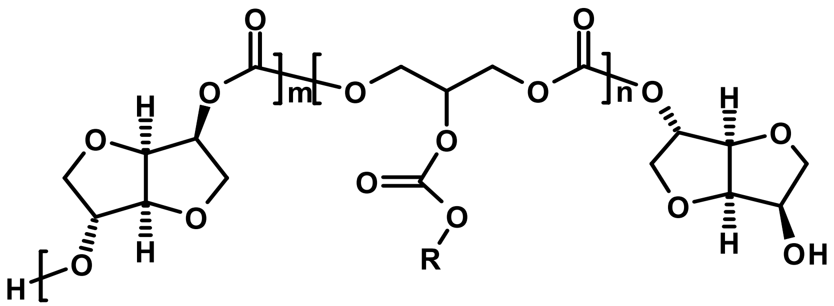
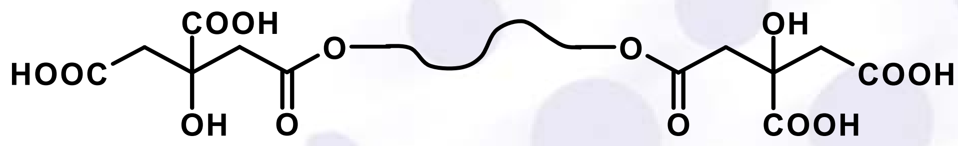
Fully biobased polycondensate resins

Branched polyesters and polycarbonates based on the
1,4:3,6-dianhydrohexitols (notably: isosorbide and isoidide)
Functionality enhanced by incorporation of, e.g., glycerol, citric acid





OH-functional polyesters / polycarbonates
(based on isosorbide / isoidide)

COOH-functional polyesters
(obtained by citric acid modification of linear OH-functional polymers)

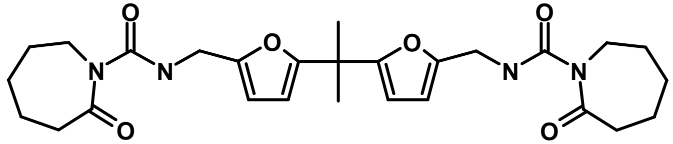
fully biobased resins with *Fn* > 2

<u>conventional curing agents:</u>
- OH-functional polymers: polyfunctional isocyanate compounds
- COOH-functional polymers: epoxy / activated OH compounds

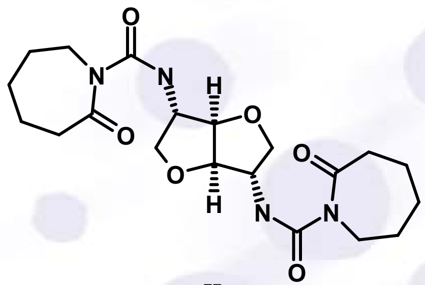
Biobased curing agents

Three novel, biobased, blocked diisocyanate compounds were developed by A&F for curing OH-functional polymers (**I – III**)

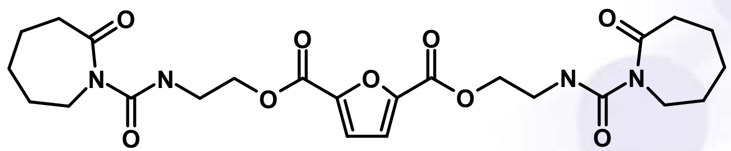
A biobased bis(glycidyl ether) was prepared by A&F to cure COOH-functional polymers (**IV**)



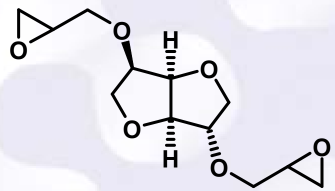
I



II



III



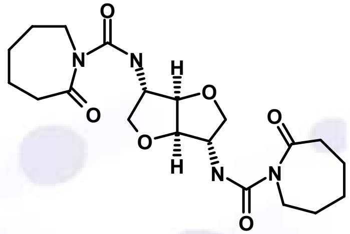
IV

I = bl-IPDFI, **II** = bl-IIDI, **III** = bl-FDEDI, **IV** = ISBGE

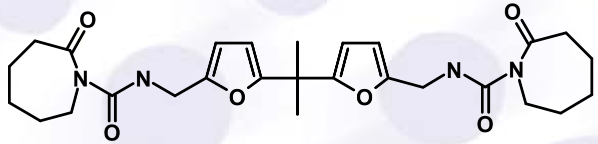
Glycerol-branched biobased resin + blocked diisocyanates
Citric acid-modified polyester + ISBGE

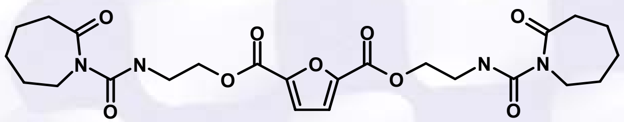
<u>Coating results:</u>

bI-IIDI: - good solvent resistance
- good impact resistance
- some discoloration

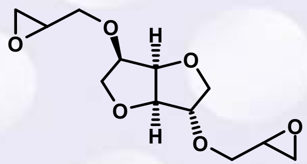


bI-IPDFI/: - moderate to good solvent resistance
bI-FDEDI - moderate impact resistance
- strong discoloration





ISBGE: - moderate to good solvent and impact resistance
- some discoloration




From bio-feedstock provided by mother earth high quality performance products can be developed

Using enzymes for developing novel polymer materials

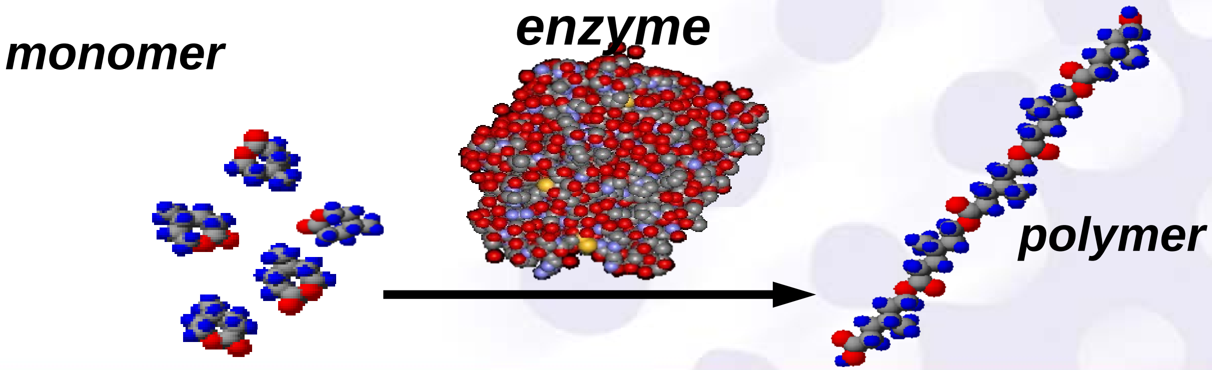
Core program DPI project #381,
continued within TA-BI, project #608 , Inge v.d. Meulen

M. de Geus, B. van As, J. Peeters, A.R.A. Palmans, A. Heise, C.E. Koning

Laboratory of Polymer Chemistry

Laboratory of Macromolecular and Organic Chemistry

Technische Universiteit Eindhoven



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Advantages of Enzymes

- *Enzymes are very efficient catalysts.*
- *Enzymes act under mild conditions.*
- *Enzymes are environmentally acceptable and metal-free.*
- *Enzymes are not bound to their natural role.*
- *Enzymes can catalyze a broad spectrum of reactions.*
- *Enzymes are selective (*chemo-, regio-, enantioselective).

These advantages can be utilized to make materials especially for biomedical applications in view of absence of metal residues, not easily available from conventional techniques.

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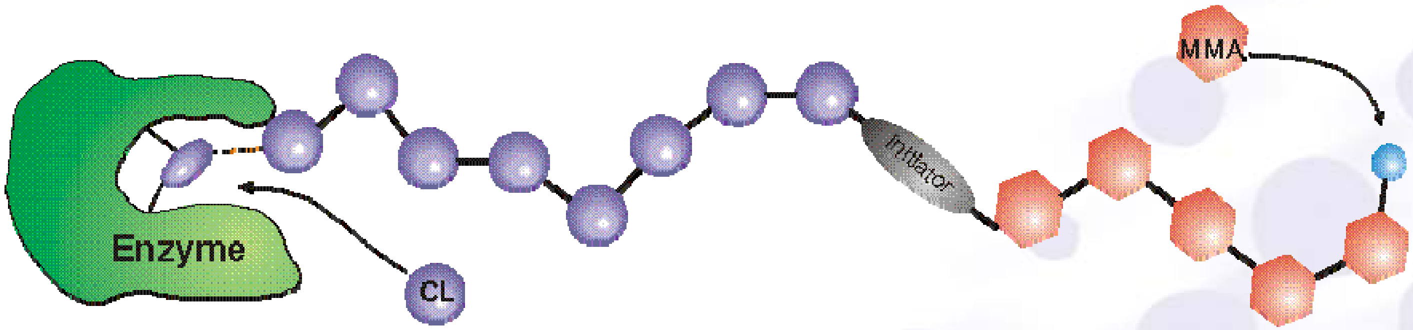
Two questions

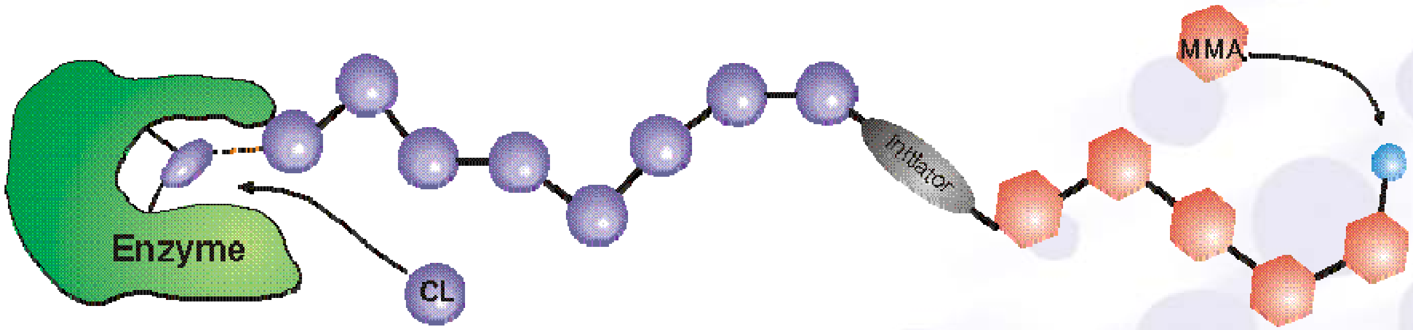
1. **Can enzymes be used in combination with chemical catalysts e.g. for the synthesis of block copolymers, and can this be realized in one pot?**



2. **Can enzymes result in materials that cannot be made using chemical catalysts?**

Two questions

1. **Can enzymes be used in combination with chemical catalysts e.g. for the synthesis of block copolymers, and can this be realized in one pot?**

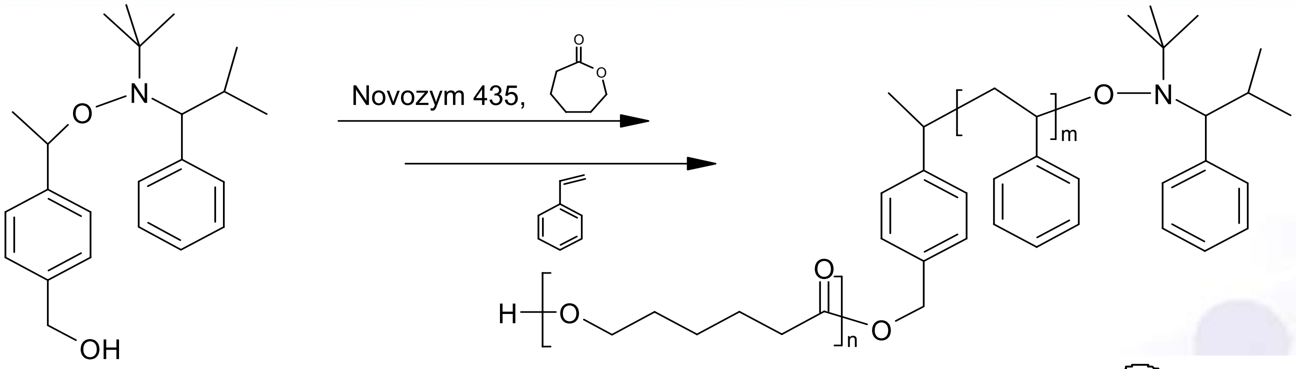


Yes

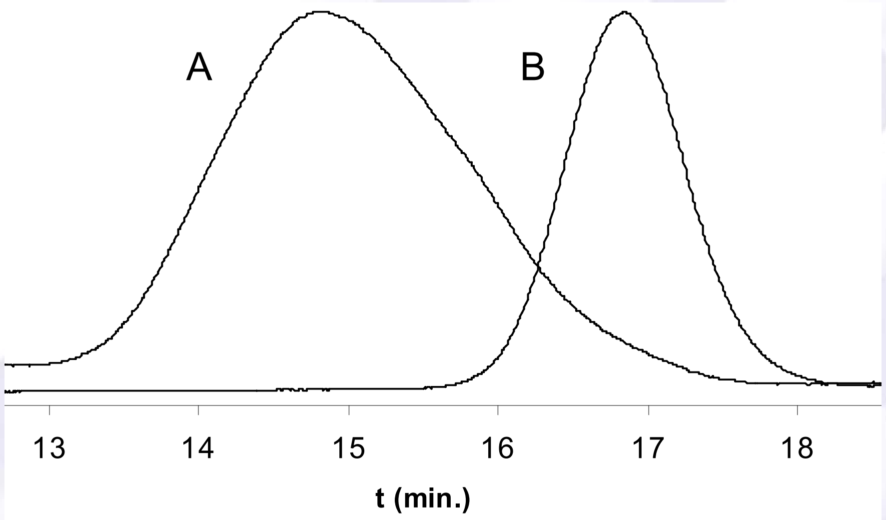
2. **Can enzymes result in materials that cannot be made using chemical catalysts?**

Yes

eROP and Nitroxide Mediated LFRP



- **Chemoenzymatic block copolymer synthesis was achieved in one pot.**
- **Method to synthesize block copolymers in a metal free fashion.**



First example of a one-pot chemo-enzymatic cascade polymerization!

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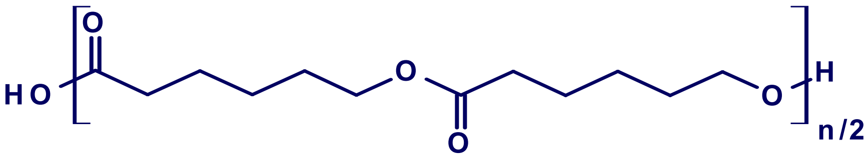
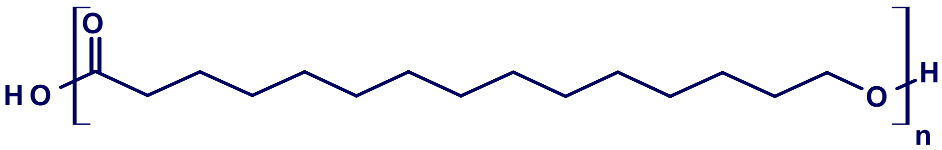
Polypentadecalactone:

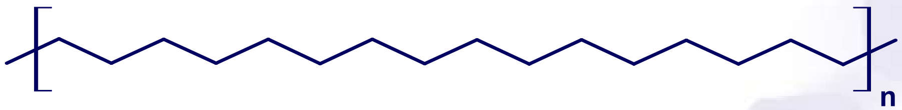
biodegradable polyethylene?



Polycaprolactone - PCL



Polypentadecalactone – PPDL
(100% linear)



Polyethylene

Properties ‘enzymatic’ PPDL (M_w= 190 kg/mol)

Non-oriented samples	T_g [°C]	T_m [°C]	T_c [°C]	E [MPa]	ε_{break} [%]	σ_{yield} [MPa]
PPDL	-20	95	81	420	>1200	18
PCL	-60	54	42	350	60	16

Chemically catalyzed synthesis of PPDL: $M_{w,max}$ = 40.000 g/mol
Enzymatically (literature) : $M_{w,max}$ = 80.000 g/mol
After careful drying the enzyme (this study): $M_{w,max}$ = 190.000 g/mol
→ (Biomedical) fiber applications come within reach (Evaluation with Bert Joosten, Marco Marcus and Ronald Deumens of AZM Maastricht)

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First results fiber spinning from melt

Melt spinning of highest molecular weight PPDL, followed by drawing/elongation results in fibers with strength of 0.6-0.7 GPa (Commercial Nylon fibers: ca. 1 GPa)

Solution spinning is expected to yield even higher strength (experiments in progress in collaboration with Lemstra)

[1] C.M. Byrne et al, J. Am. Chem. Soc., 126, 11404-11405 (2004)

Degradability needs optimization if biomedical applications are targeted (copolymers with more hydrophilic comonomers and reduced crystallinity)

Inge van der Meulen (DPI #)

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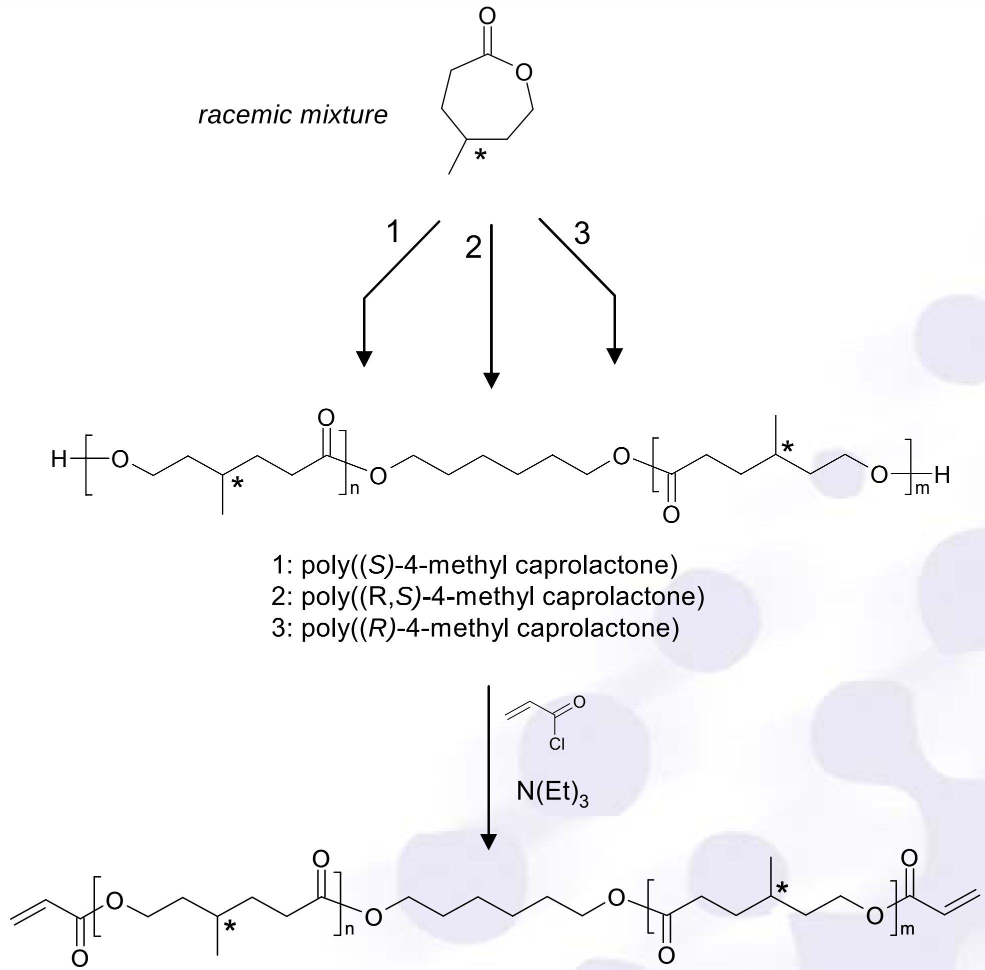
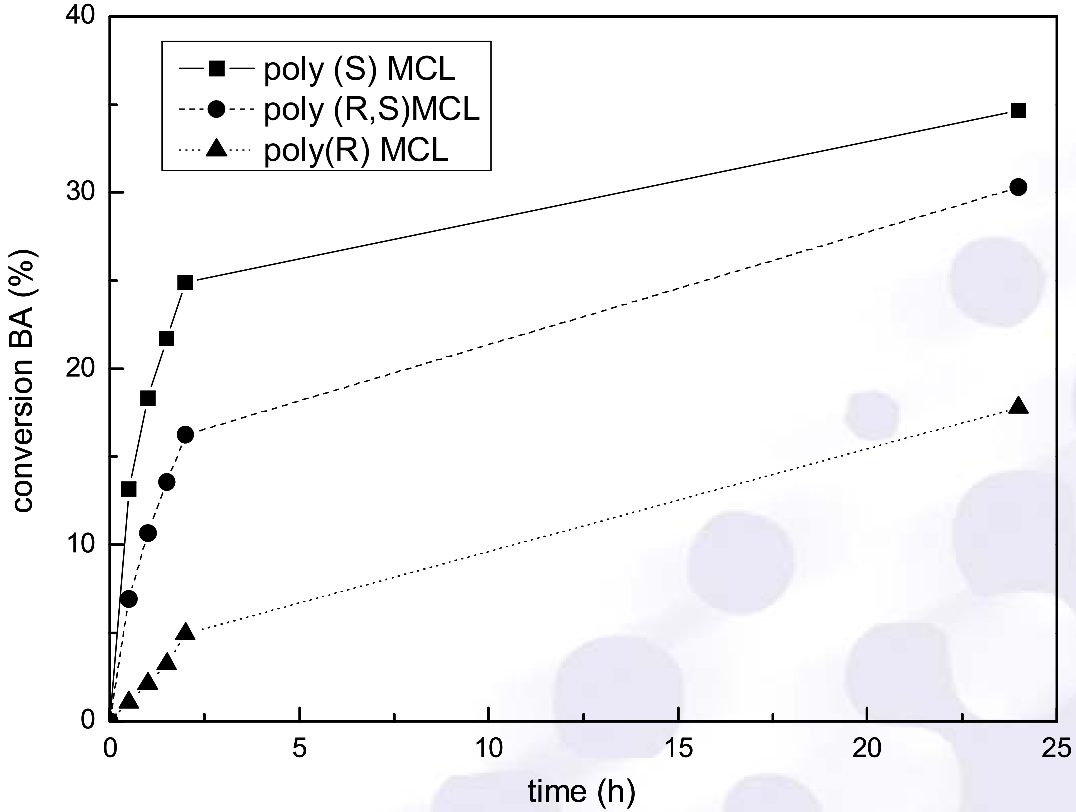
Chiral polyester particles for drug release

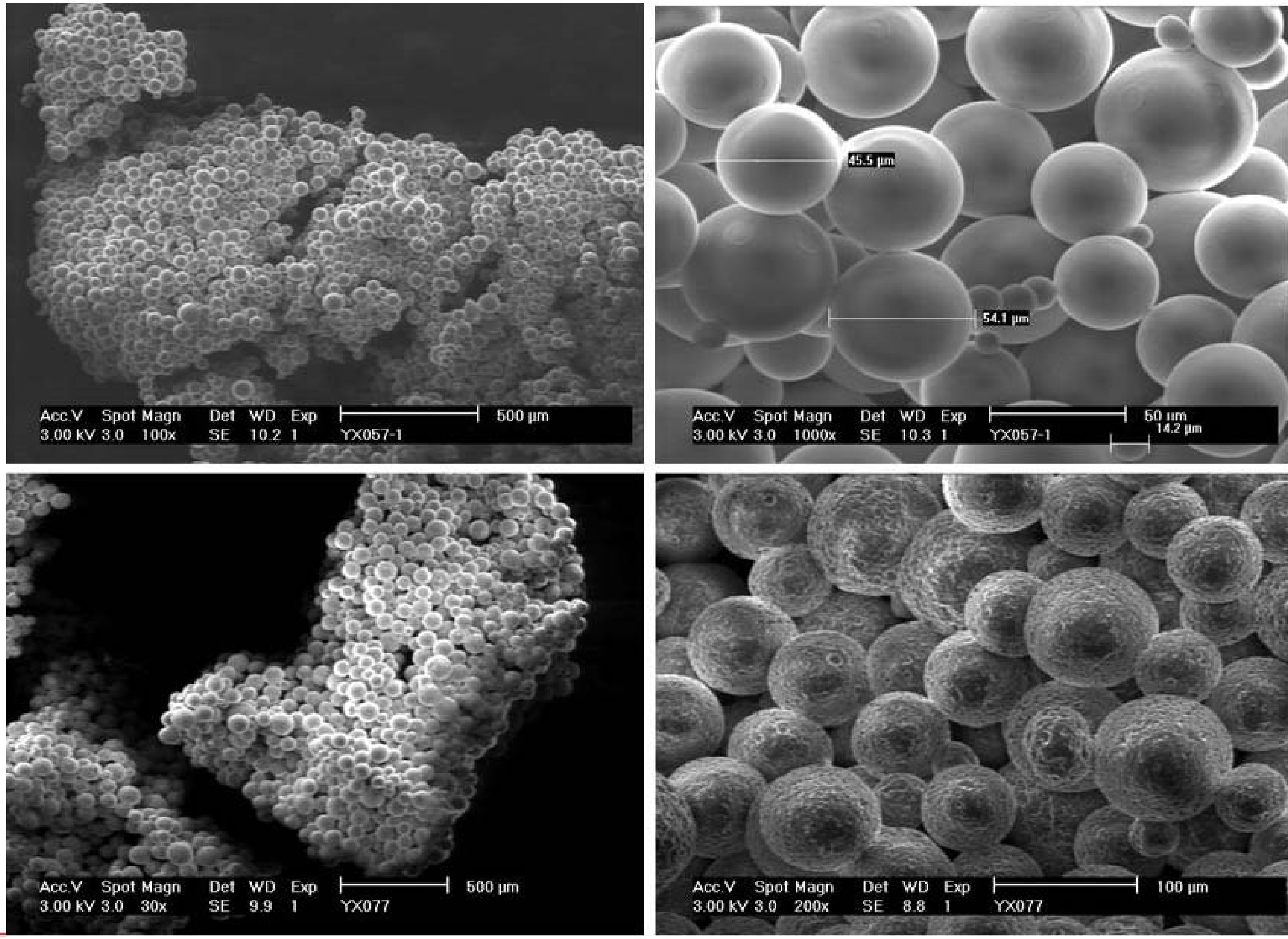


Jenny Xiao, Andreas Heise, Anja Palmans ‘Biomade’



Novozym 435 catalyzed degradation of chiral and racemic PMCL

UV-cured poly(4-Methyl CL) particles



Mother earth provides bio-catalysts suitable for development of high quality performance products

Carbon-Nanotube/Polymer Composites:

Starting Wetter, Conducting Better

A latex-based concept to develop electrically conductive Polymer/carbon nanotube composites

TAs EP/RT + FPS, projects 416 and 529

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- Nadia Grossiord, Marie-Claire Hermant, Bert Klumperman, Junrong Yu, Kangbo Lu, Joachim Loos, Jan Meuldijk, Alex van Herk, Paul van der Schoot

  Eindhoven University of Technology, The Netherlands

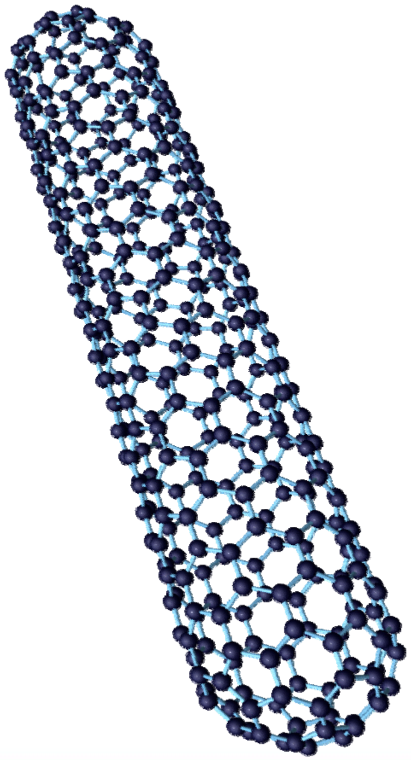
- Oren Regev

  Ben-Gurion University of the Negev, Israel

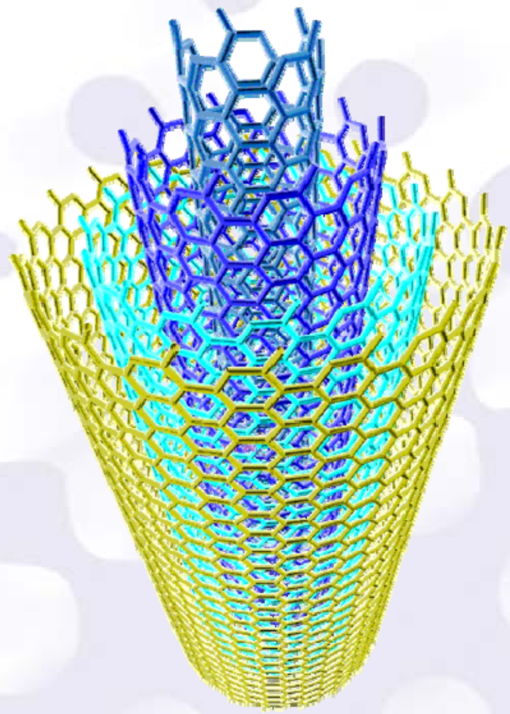
- Hans Miltner, Bruno Van Mele

  Free University of Brussels, Belgium

Single vs. Multi-Wall Nanotube



vs.



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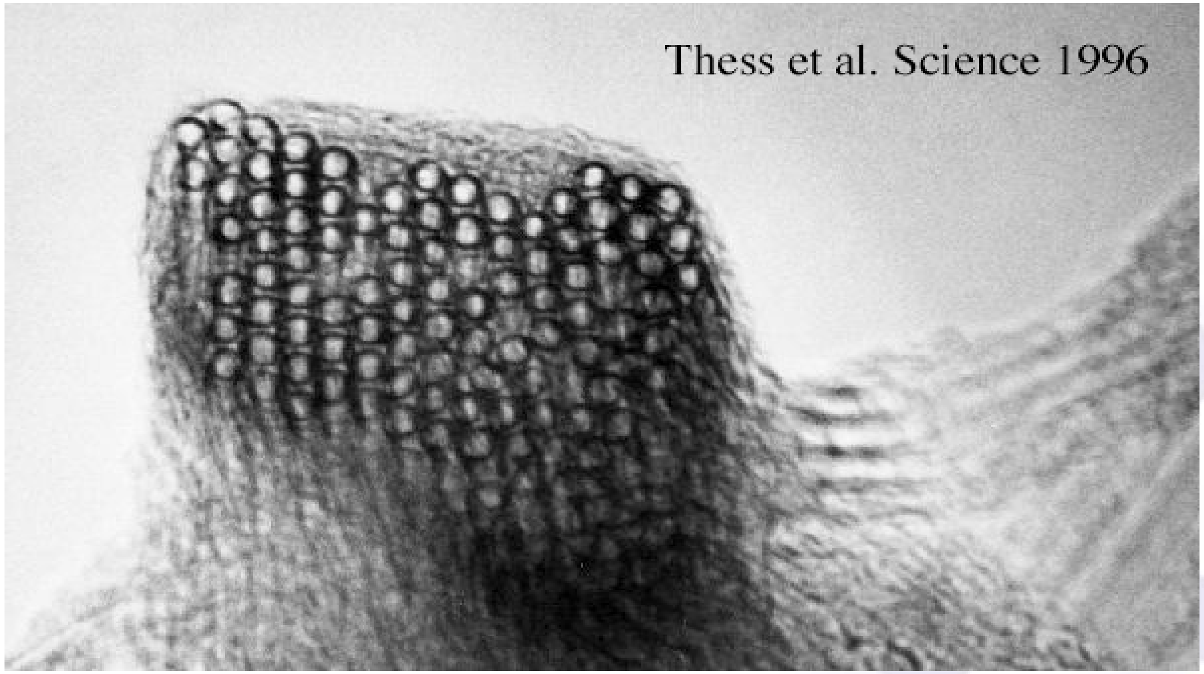
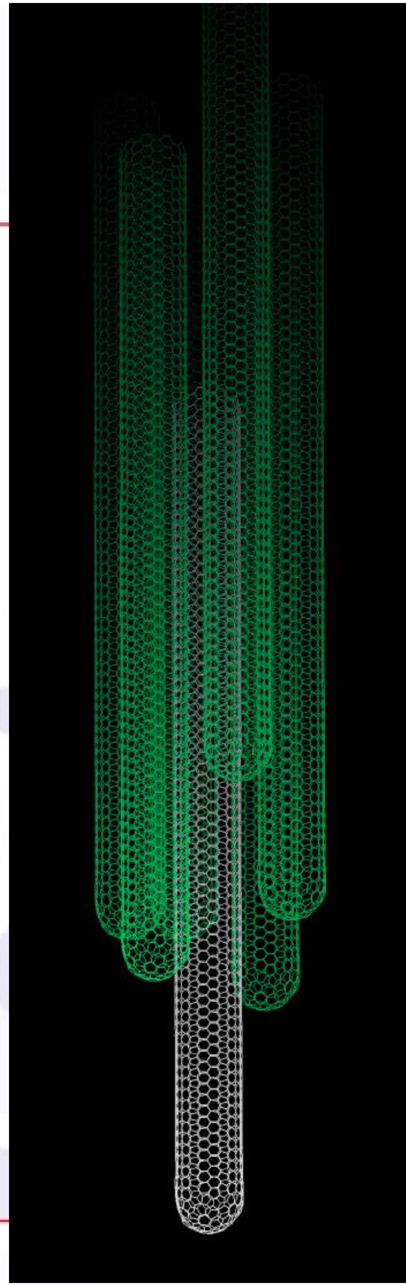
Promising fillers for polymer composites

- Low loading can give percolation because of high aspect ratio
- Strong and stiff
- Good electrical conductivity

Bundled (SW) or entangled (MW)

A bundle of nanotubes





Production of the composite

1st step Make stable aqueous CNT dispersion

1. Bring the NTs in contact with SDS (sodium dodecyl sulphate) surfactant solution
2. Sonication for debundling (15 min, 20W, 20kHz)
3. Centrifugation of catalyst residues (30 min, 4000 rpm) and continue with supernatant

2nd step: **Mixing** of the **NTs** solution with the **polymer latex**

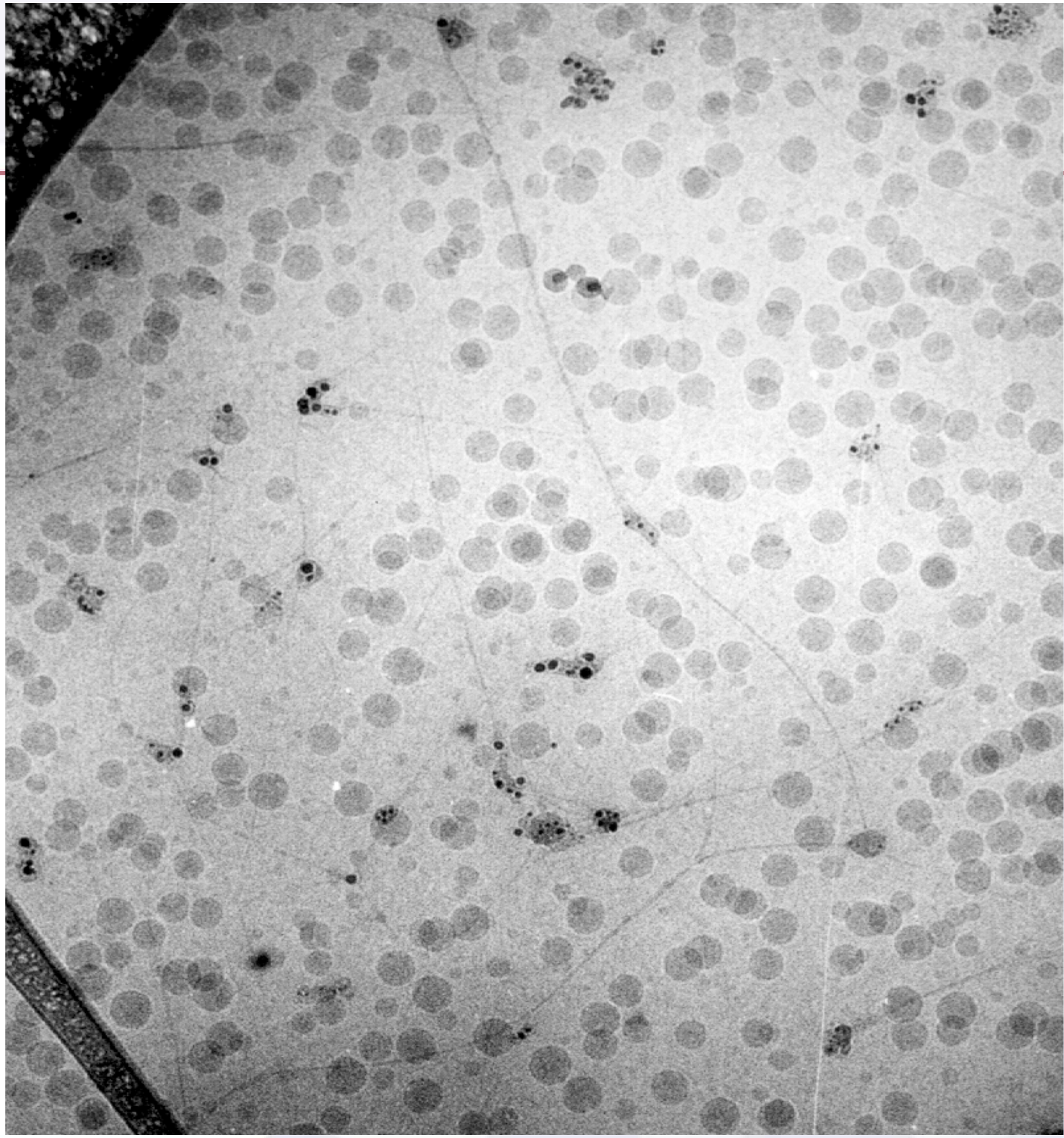
3rd step: **Freeze drying** of the mixture

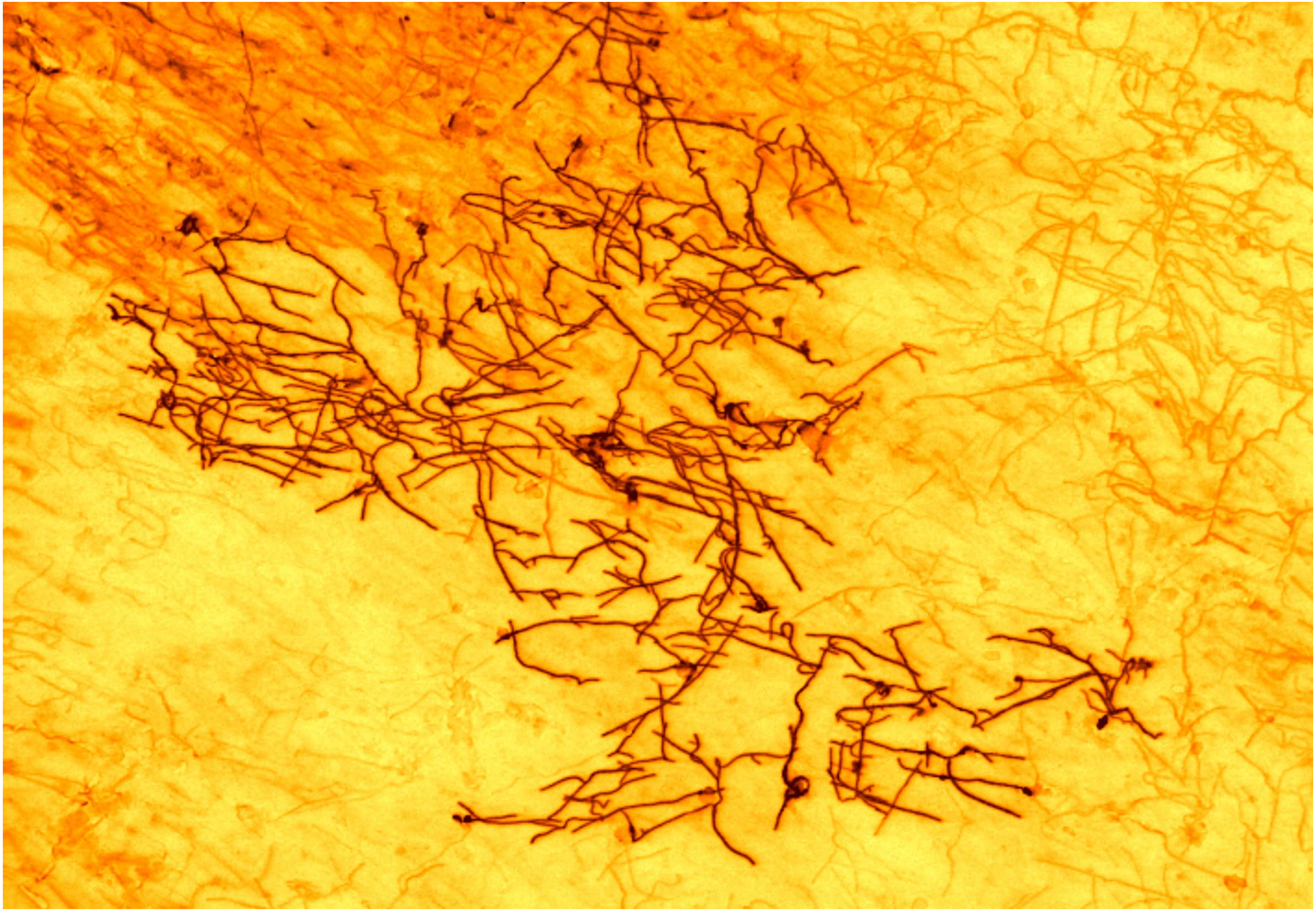
4th step: **Melt Processing** of the powder obtained

Step 2
Mix NTs and latex

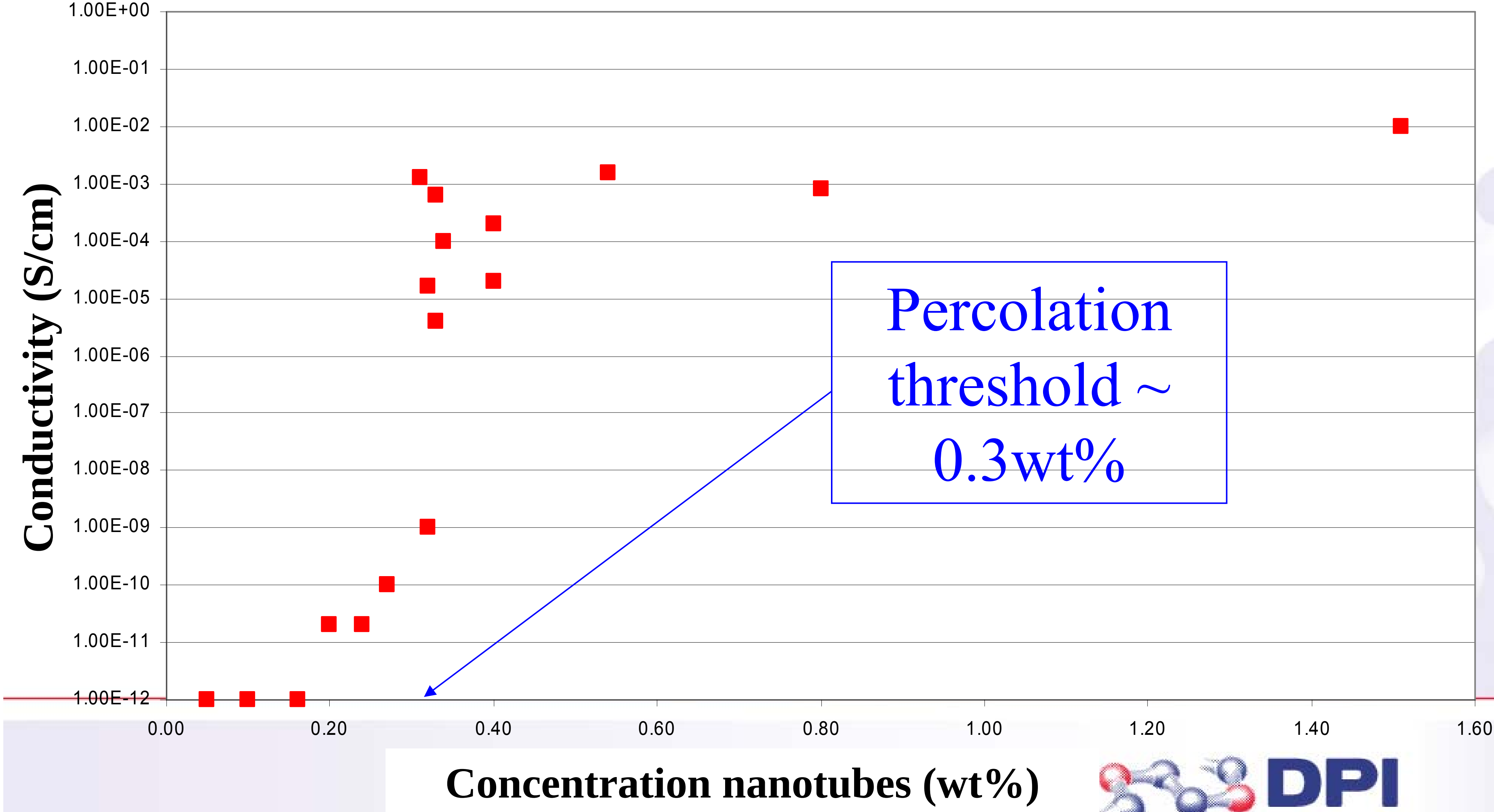
Both NTs and PS latex particles stabilized by SDS

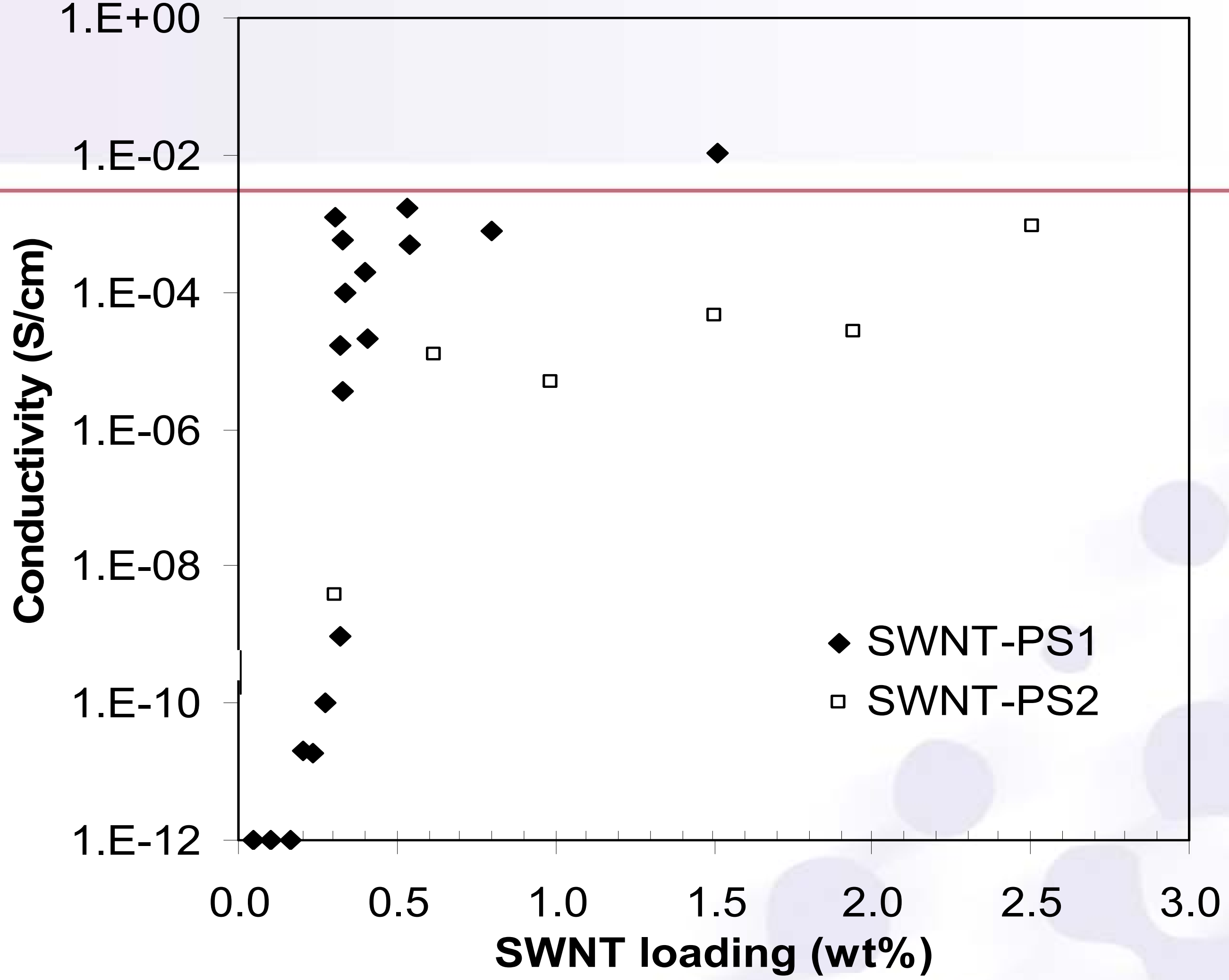
$\Phi_{av,latex} = 70$ nm





PS-SWNT composite





Nadia Grossiord et al., *Chem. Mater.*, 2007

4-point measurements. Addition of 2-3 wt% ‘PS’ with DP=5 to nanocomposite PS-2 with 1 wt% SWNT roughly raises conductivity by a factor 10 (2-point)

Question

How versatile is the latex concept?

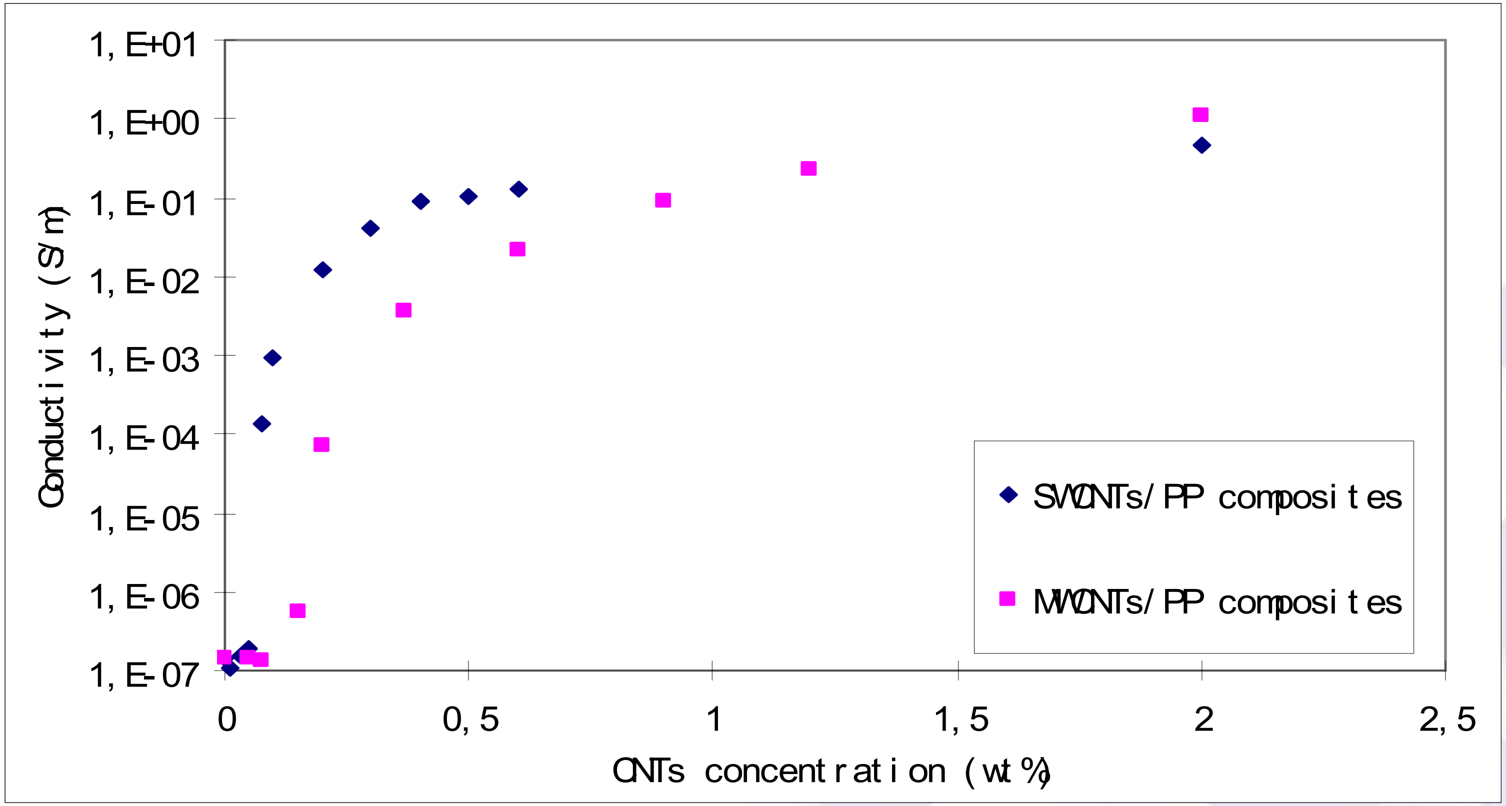
Question

How versatile is the latex concept?

It works for PS, ABS, PMMA, PP, PE, PUR, PS/PPE, and PVC latexes.

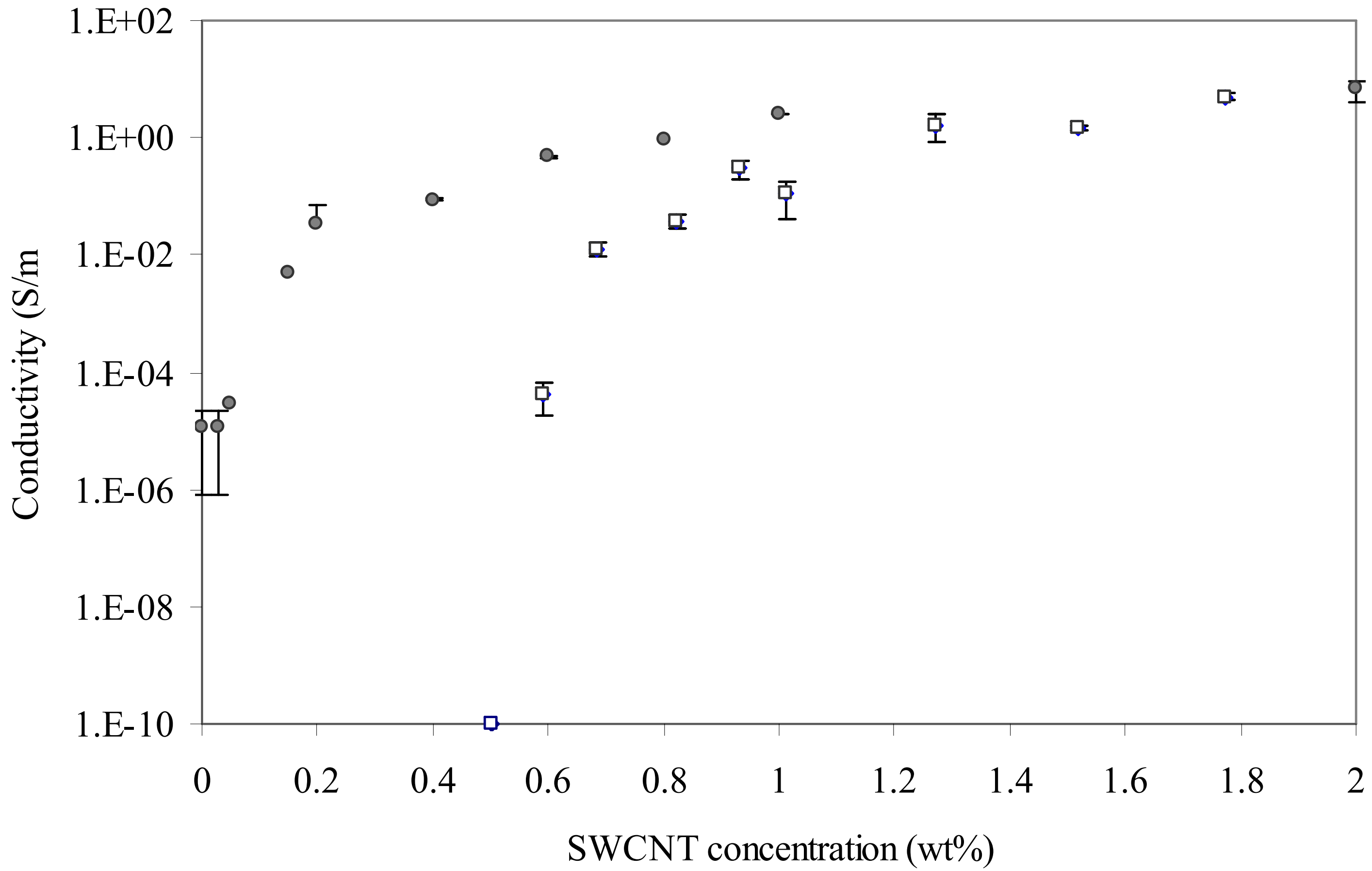
So, virtually all polymer latex particles can be applied.

Polypropylene/CNT nanocomposites (semi-crystalline)



2-point conductivity measurements of Priex 801 + HiPCO SWNTs and Priex 801 + thin MWNTs of Nanocyl.

Four-point conductivity measurements as a function of the SWCNT concentration for: (●) SWCNT/Priex®801 and (□) SWCNT/PS nanocomposites.



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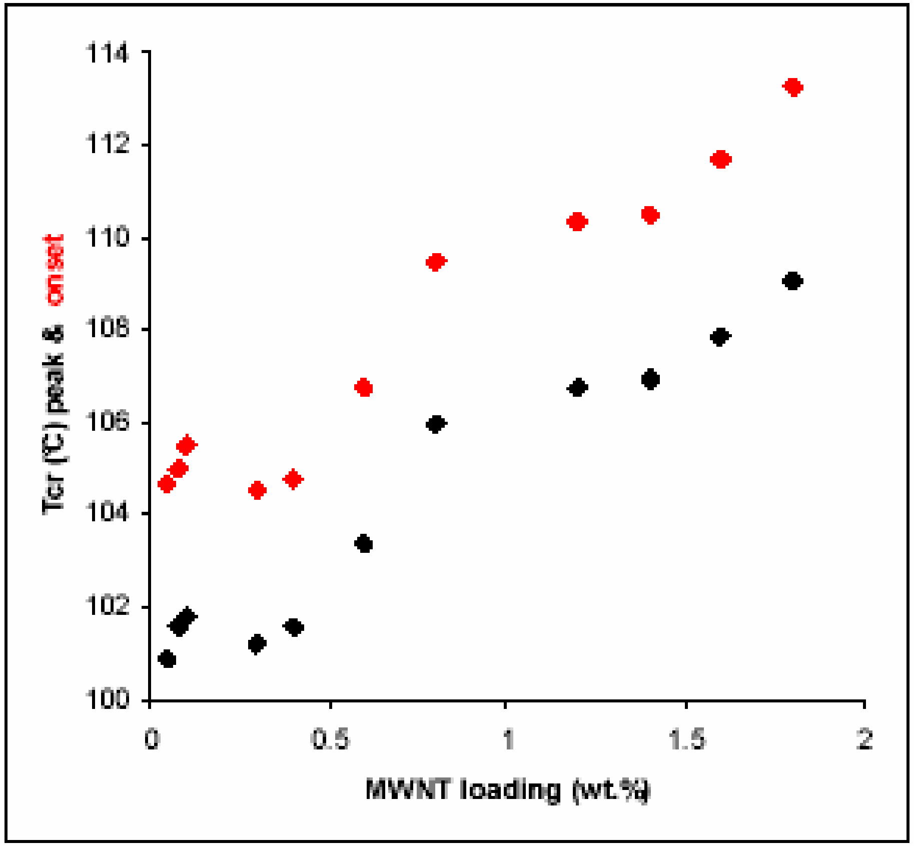
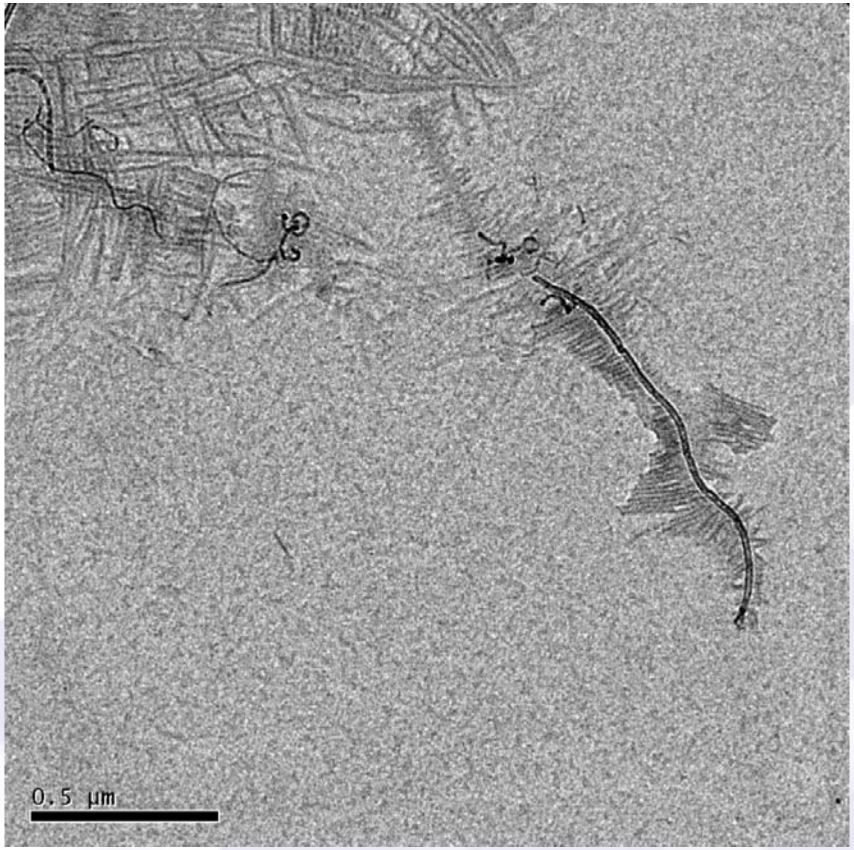
Crystallization peak and onset temperatures for various Priex 701 / MWNT samples after non-isothermal crystallization from the melt
(cooling at 2.5°C/min, temperature modulation of ± 0.5°C/60s)





Hans Miltner, Kangbo Lu, Joachim Loos

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Where and what can we improve?

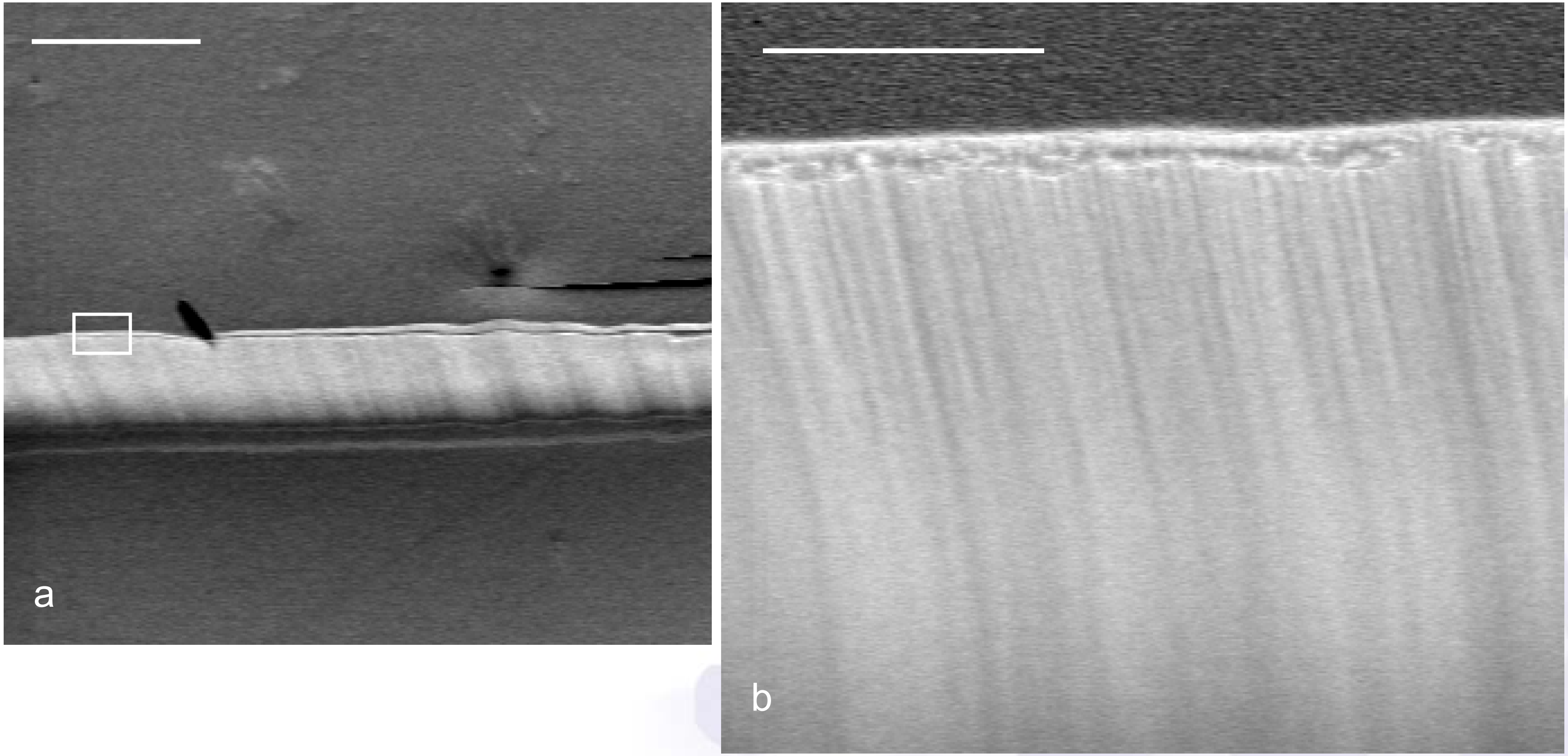
Improving dispersion is difficult or even impossible.

Therefore we focused on

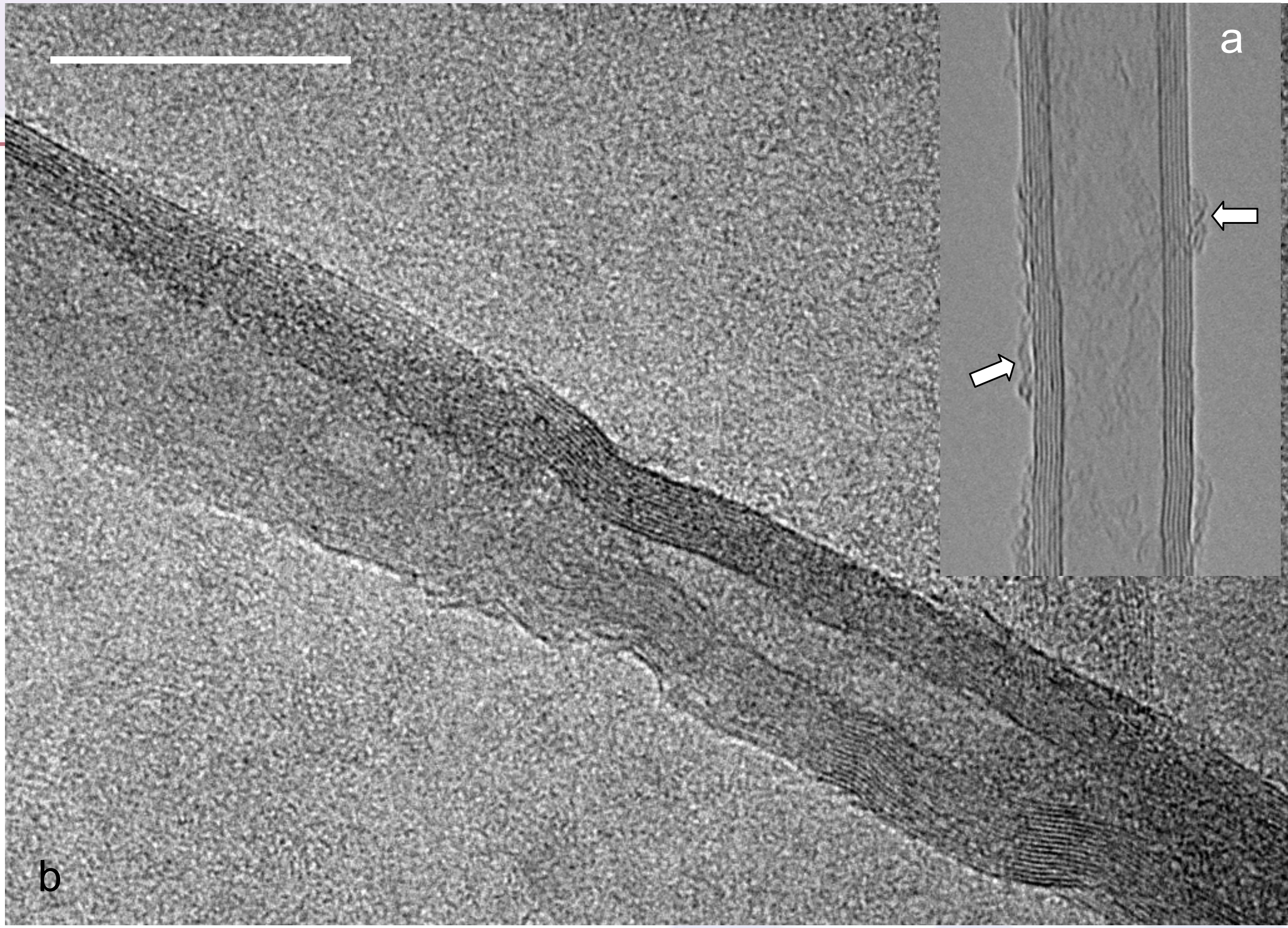
- Quality of the tubes
- Reduction of amount of CNTs by making foams
- Reduction contact resistivity by replacing surfactant SDS by conducting surfactants

as methods to reduce percolation thresholds.

Vertically grown MWNTs (John Hart, MIT)



Scale bars: (a): 250 μm; (b): 50 μm



HRTEM (High Resolution TEM) photos

(a): picture of a vertically-grown MWNT (MIT)

(b): commercially available MWNT (Nanocyl)

Scale bar valid for both photos: 20 nm

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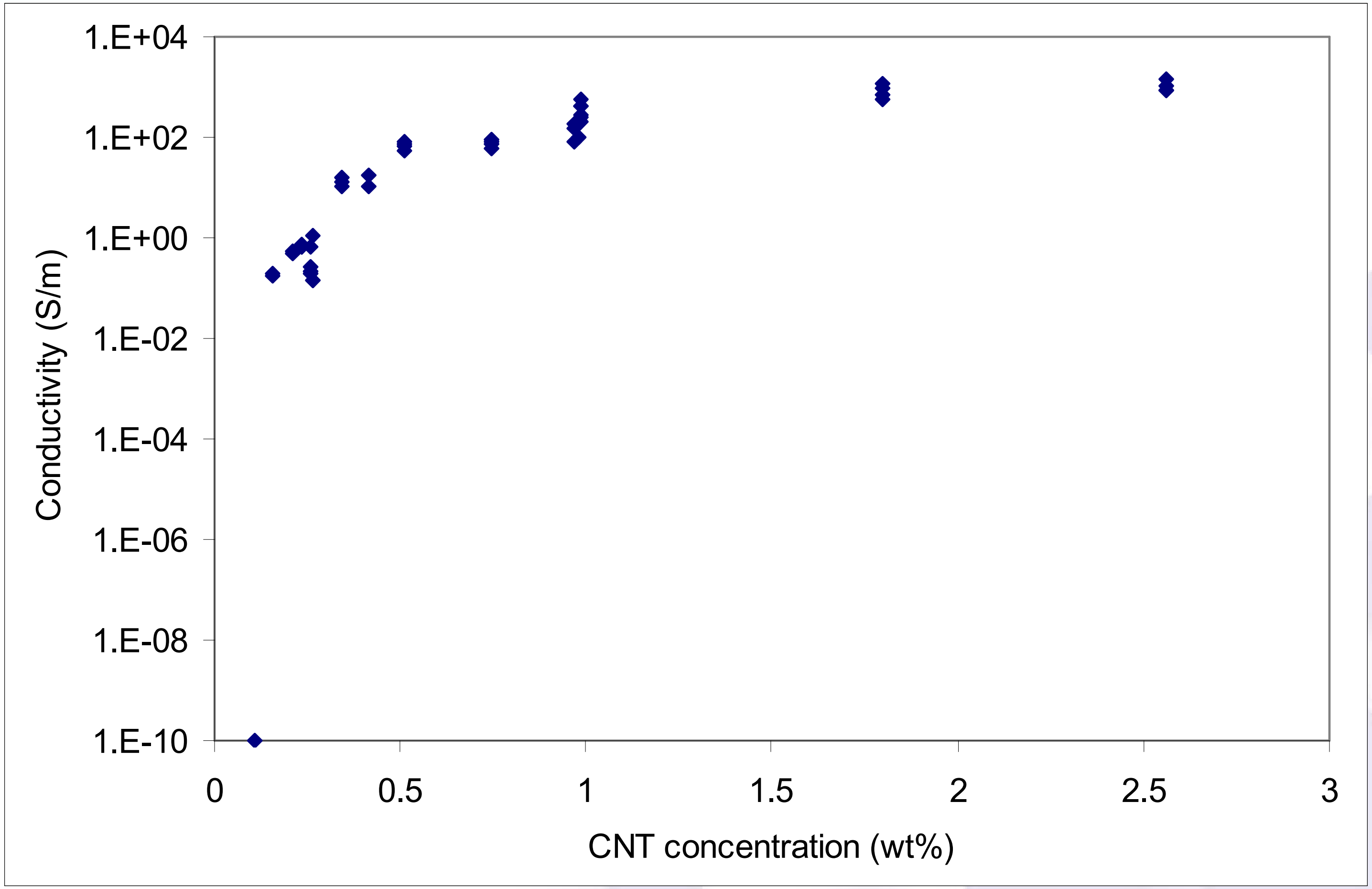
Long NTs vertically grown



Four-point conductivity of MWNT-PS composite as a function of MWNT concentration.

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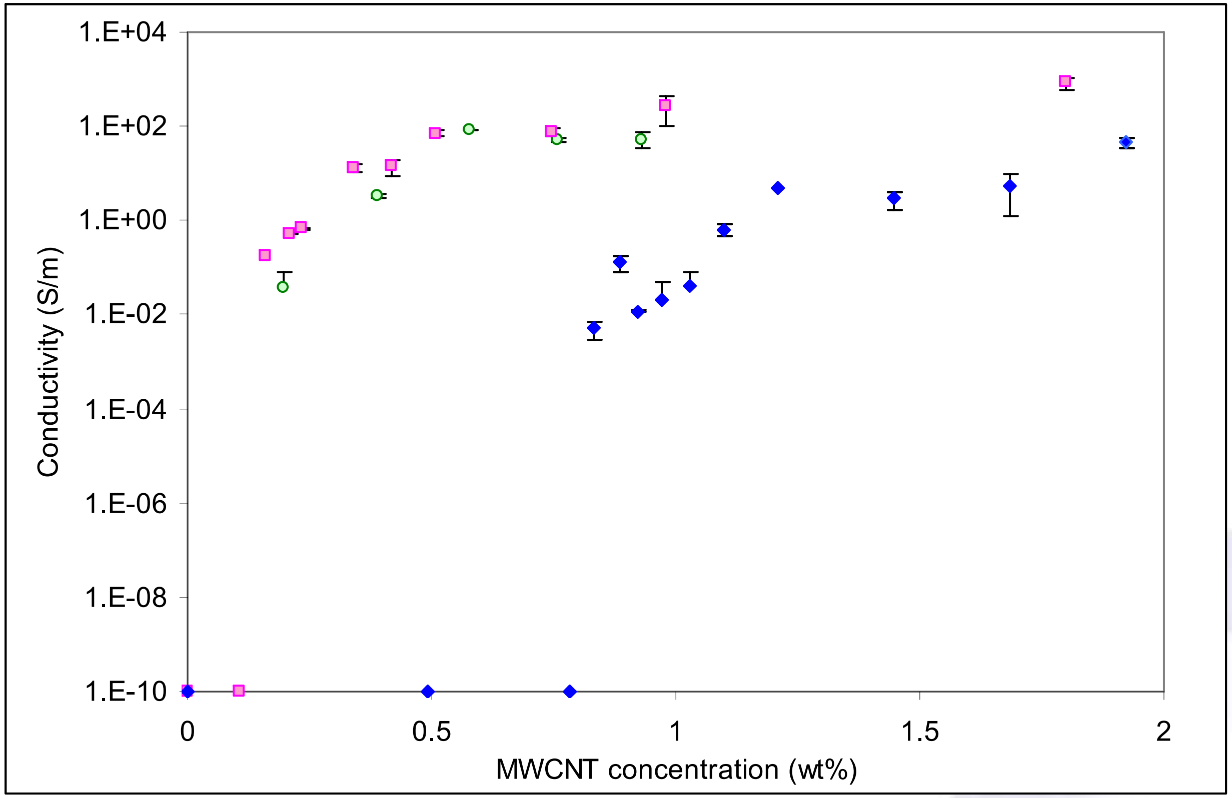
CNTs dispersed in the same PS matrix, under similar conditions.



Blue: Nanocyl MWNTs
Pink/green: vertically grown MWNTs

Vertically grown tubes are longer after incorporation into PS, and contain less amorphous carbon

NOTE: extremely high conductivity (>1000 S/m) for 1.5-2.0 wt% MWNT

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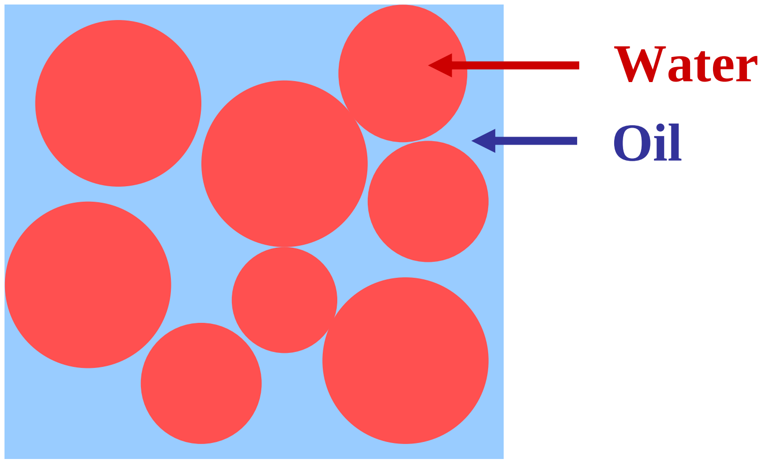
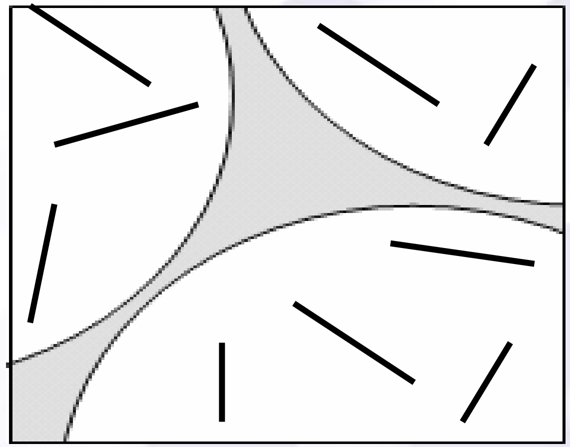
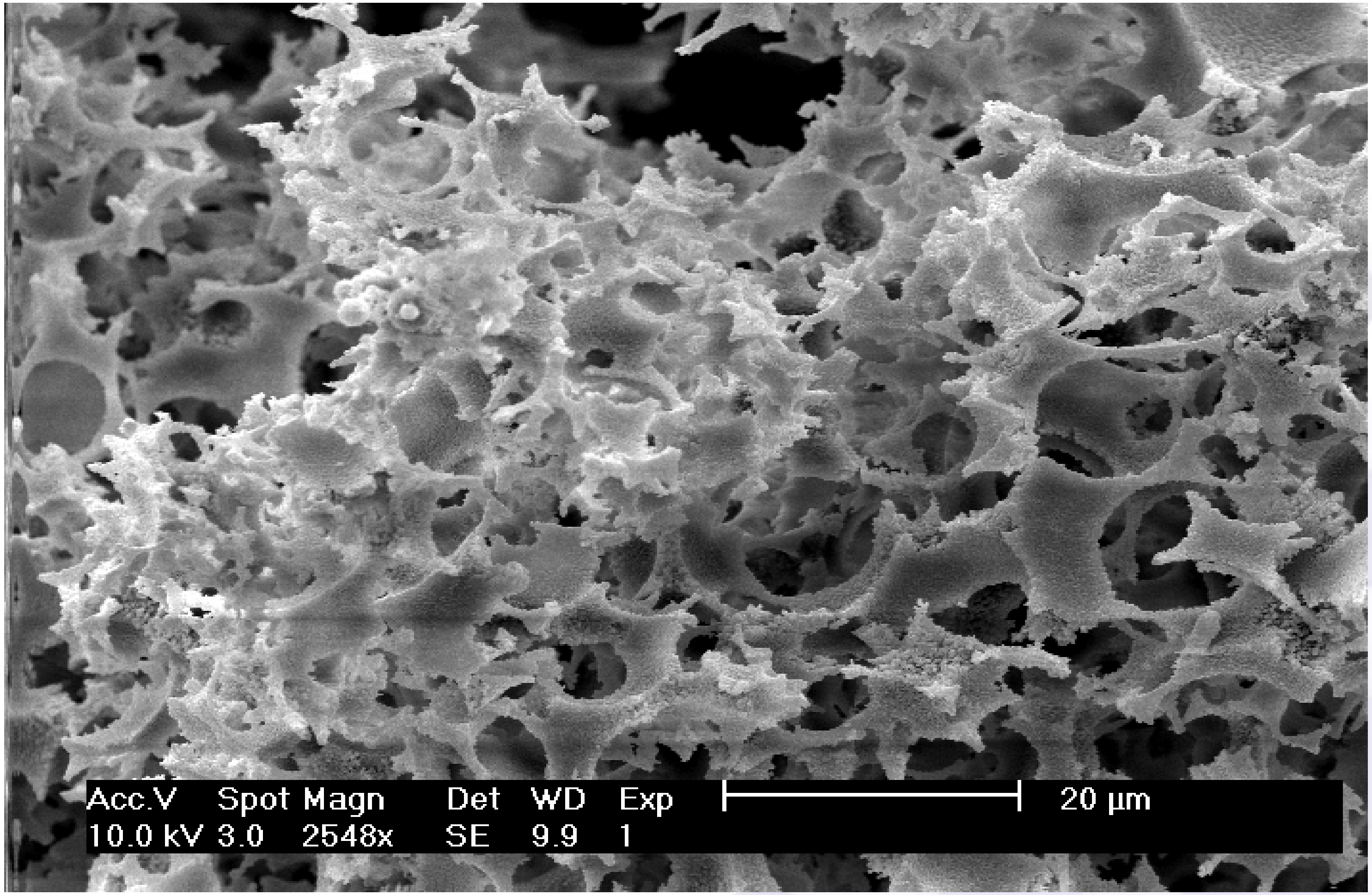
Reduction of required wt% CNTs by 'foaming'

Continuous styrene/divinyl benzene phase is polymerized
SWNTs are dispersed in water droplets

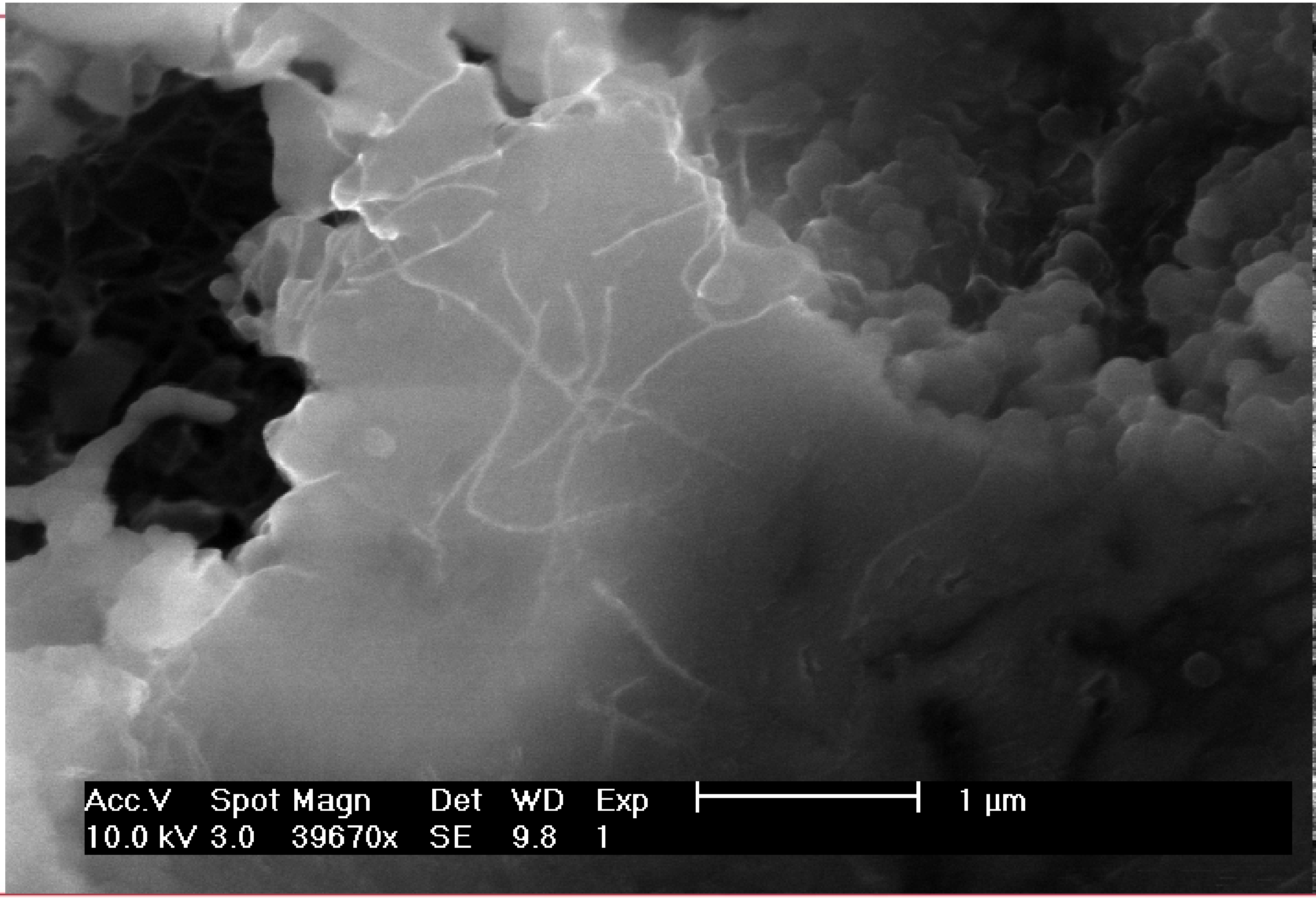




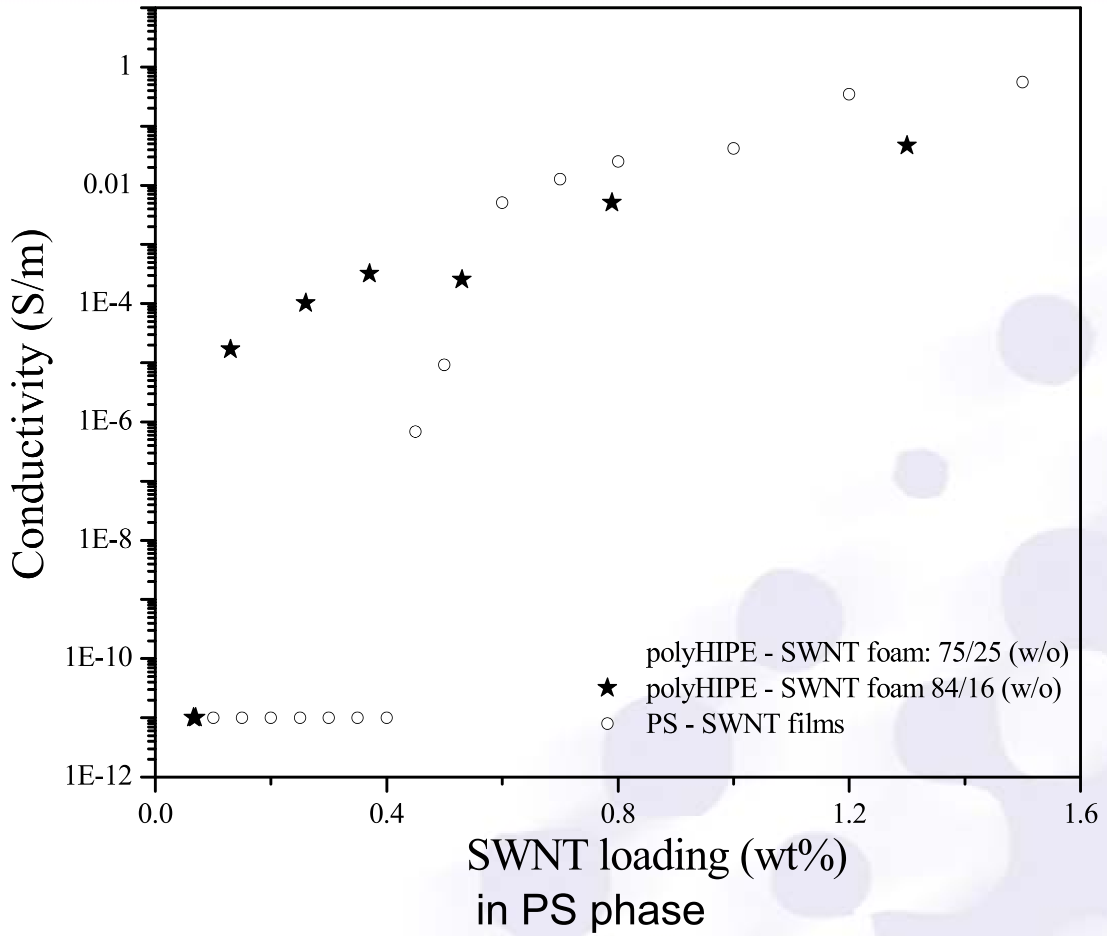
High internal phase emulsion derived PS foam



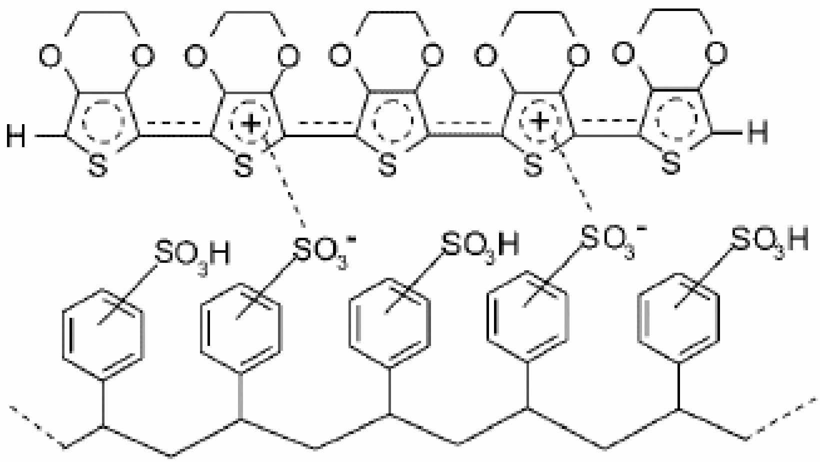
SWNTs embedded in polyHipe walls

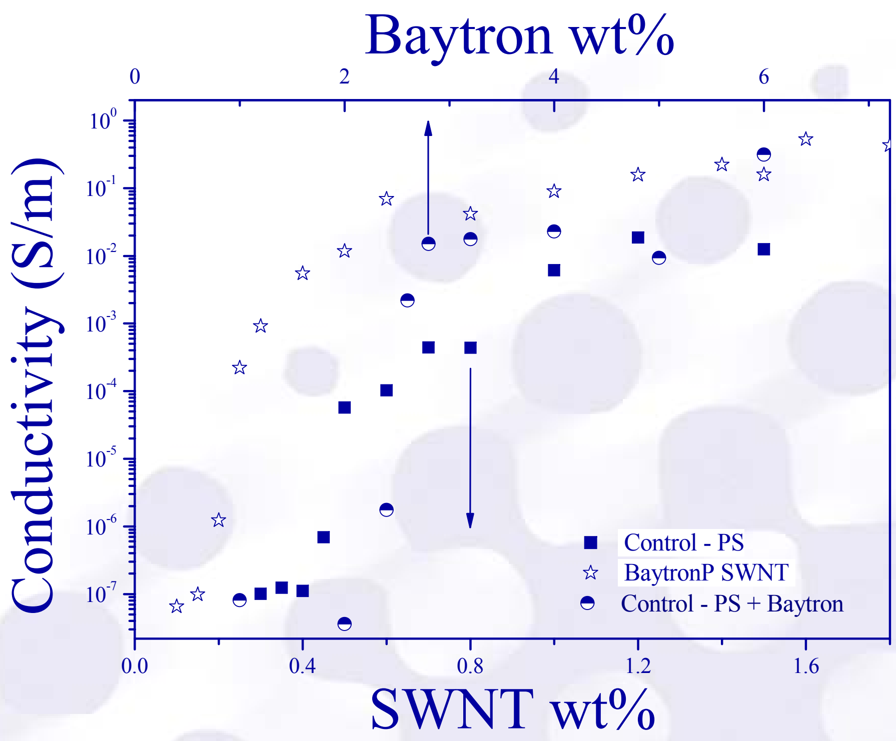


Percolation threshold reduced by factor 3 - 4



Conductive surfactants replacing SDS and lowering contact resistivity





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Water plays a crucial role in the development of polymer/ carbon nanotubes nano-composites with well-dispersed CNTs

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New coating resins based on the copolymerization of epoxides with carbon dioxide

TA-CT, DPI projects # 451 and 607

Rob Duchateau
Saskia Huijser
Bart Noordover
Marion van Straten
Wouter van Meerendonk
Maurice Frijns
Wieb Kingma

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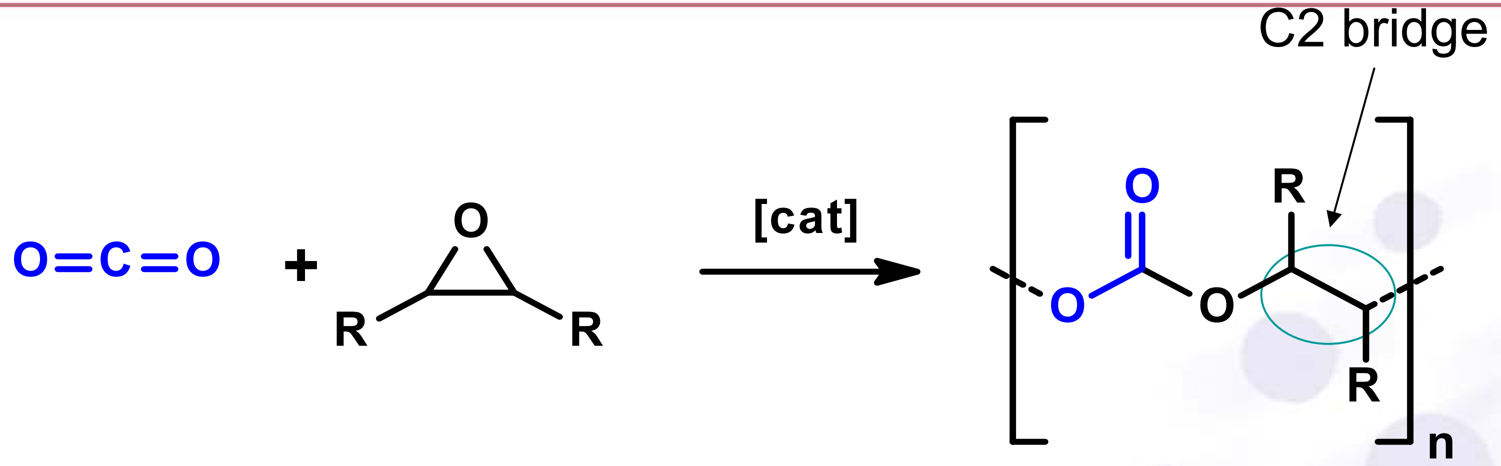
Co-polymerization of CO_2 and oxiranes

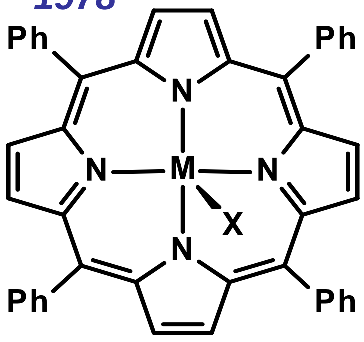


Aliphatic polycarbonates

- First discovery in 1969 by Inoue.
- Most frequently used catalysts are based on Zn, Al and Cr.
- Frequently used monomers: cyclohexene oxide (CHO), propylene oxide (PO) and ethylene oxide (EO).

Development of catalysts

1978

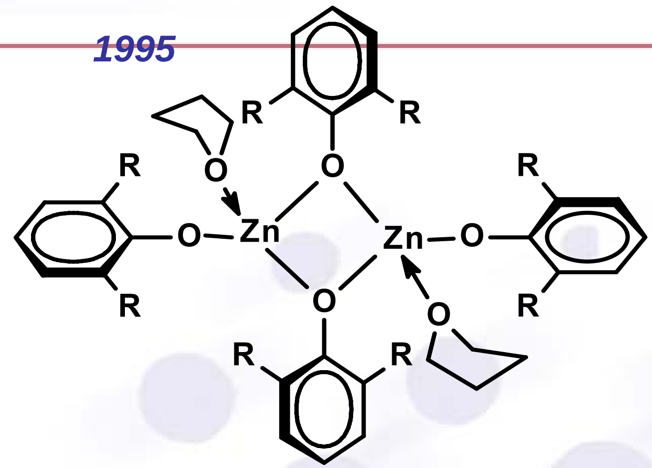


M = Al, Cr

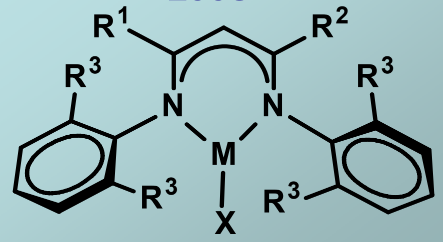
1969

$ZnEt_2 + H_2O$

1995

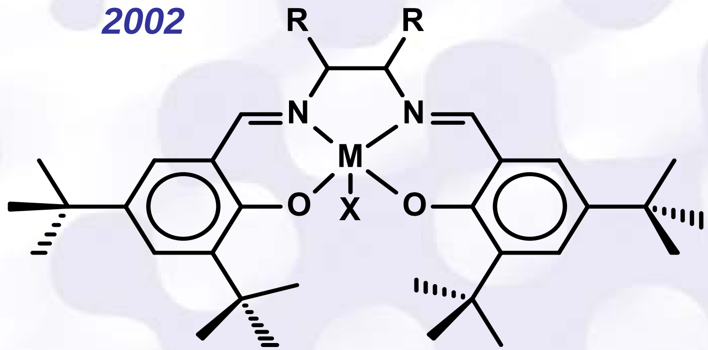


1998



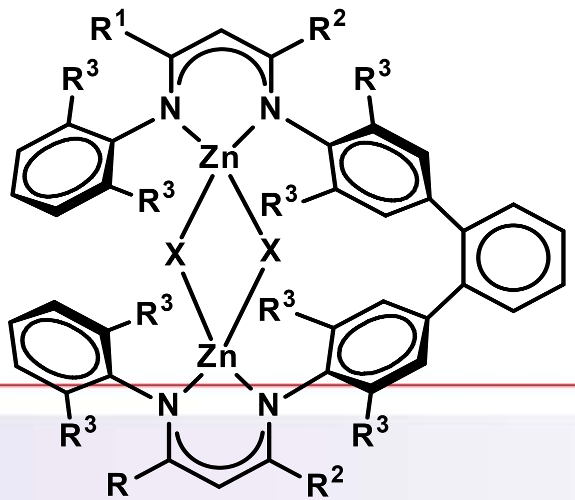
M = <u>Zn</u>, Y, La

2002

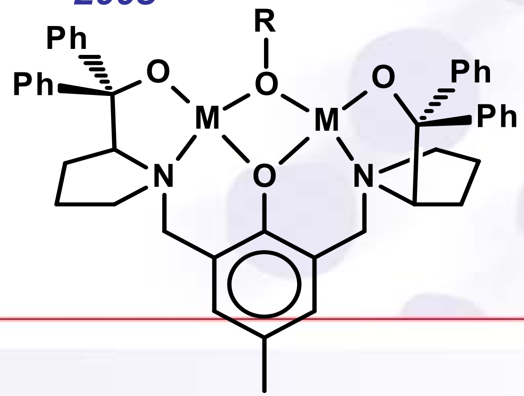


M = Al, Cr, Mn, Co

2004

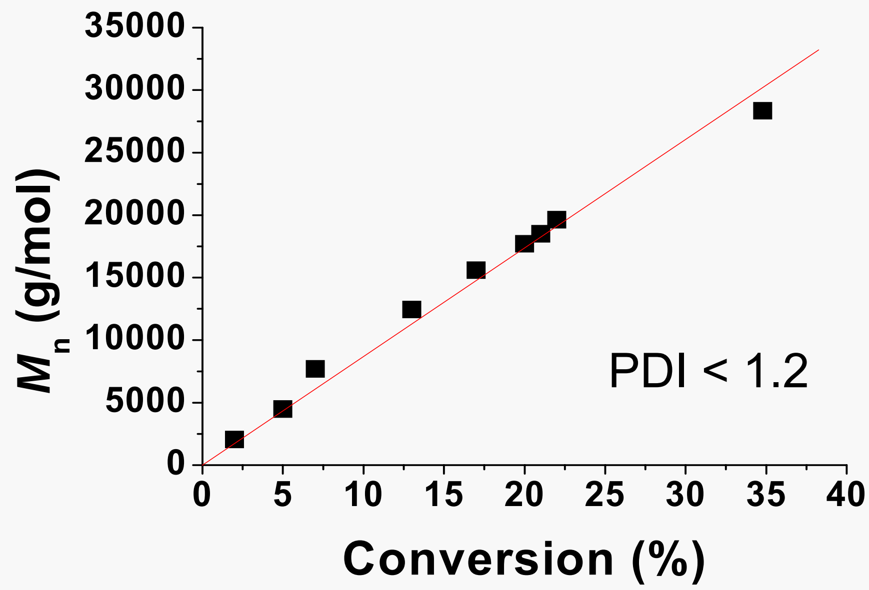


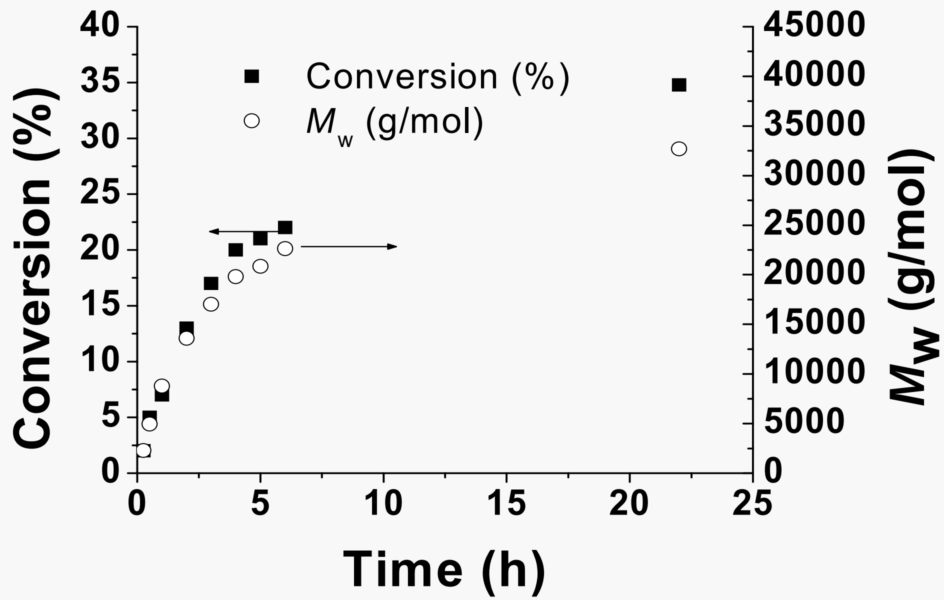
2005

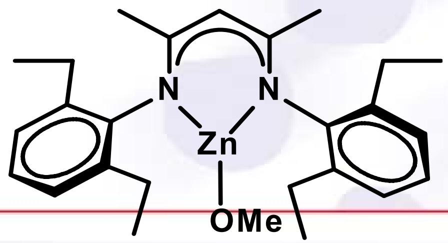


M = Zn, Mg

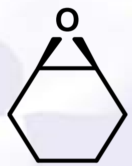
Typical reaction kinetics of β-diiminate zinc catalysts







Catalyst



Monomer

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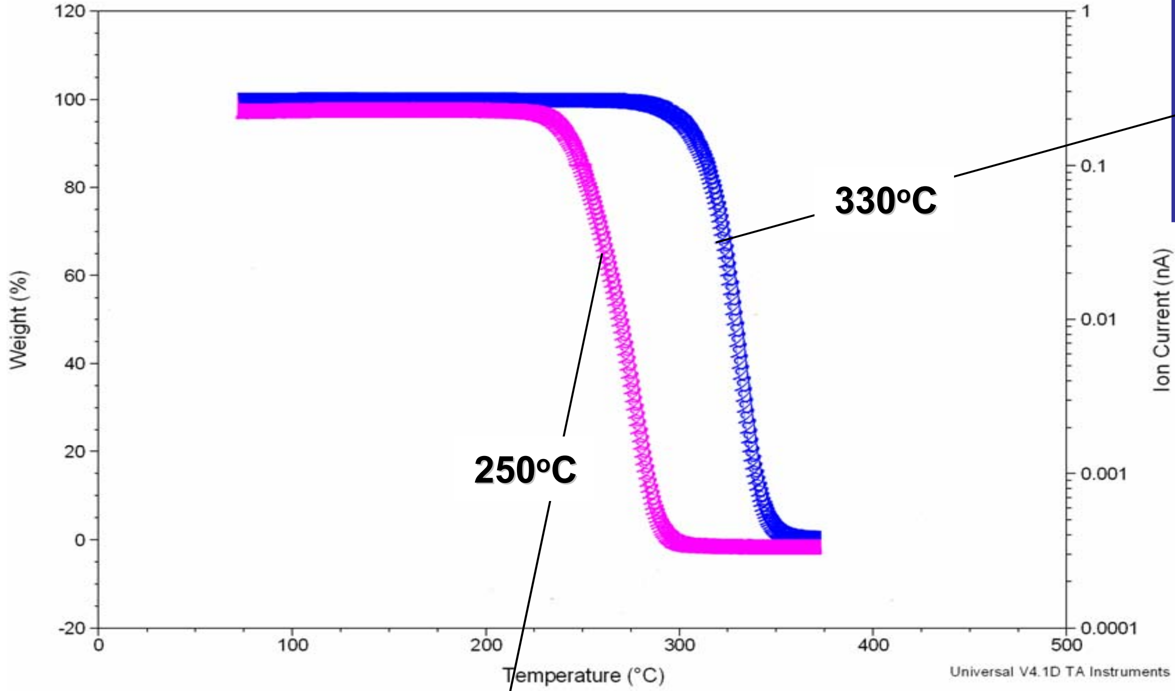
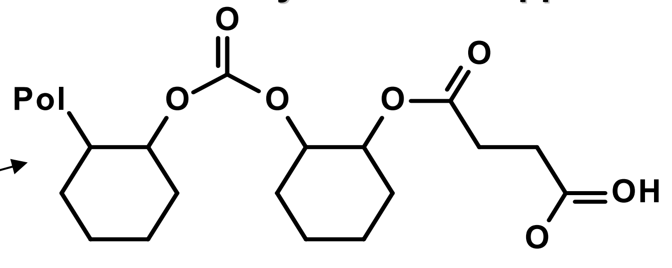
Macromol. Rapid Commun. **2004**, *25*, 382.

Properties of polycyclohexene carbonate

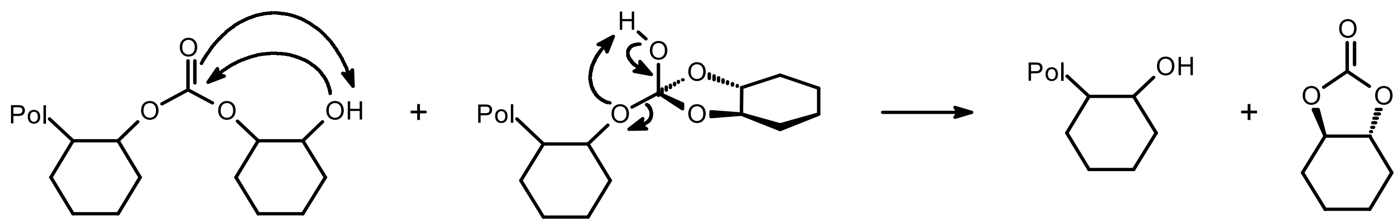
Thermal stability



Succinic anhydride end-capped



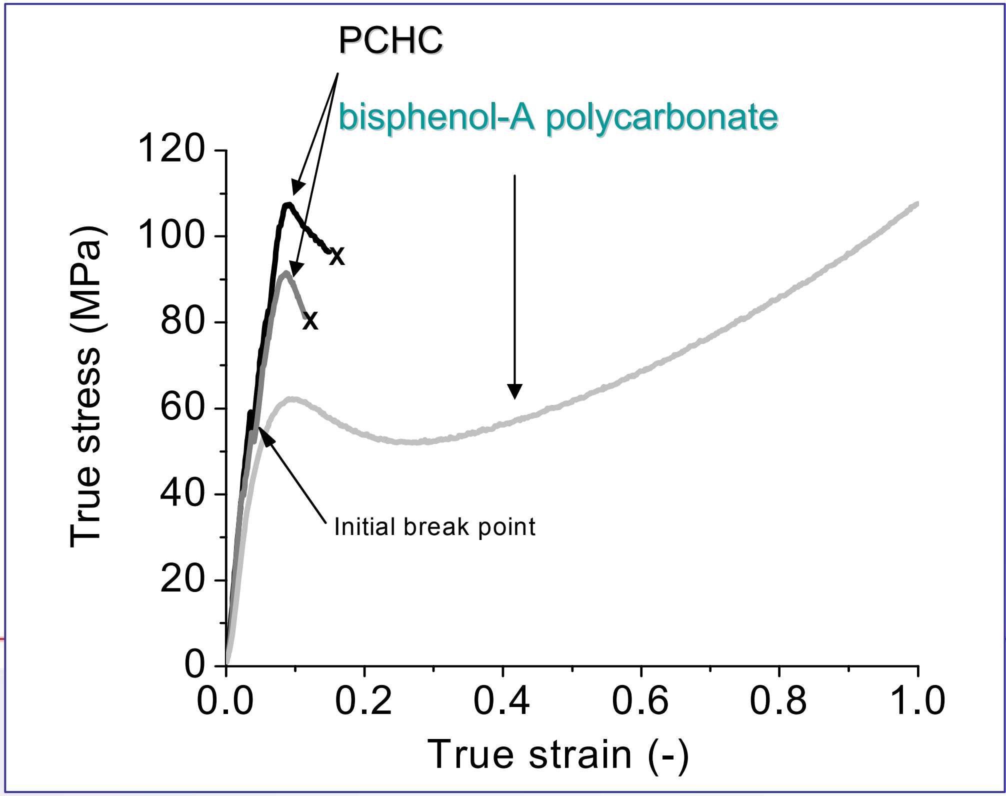
Thermal stability is significantly increased by end-capping



Properties of polycyclohexene carbonate (PCHC)

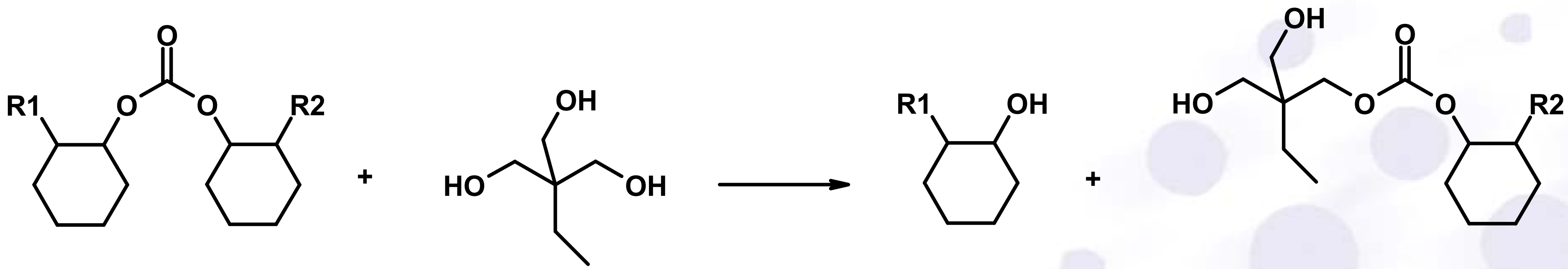
Glass Transition temperature PCHC: T_g = 116 ºC – rather low Tg prevents broad application as engineering plastic

Compression molding tests on high MW PCHC



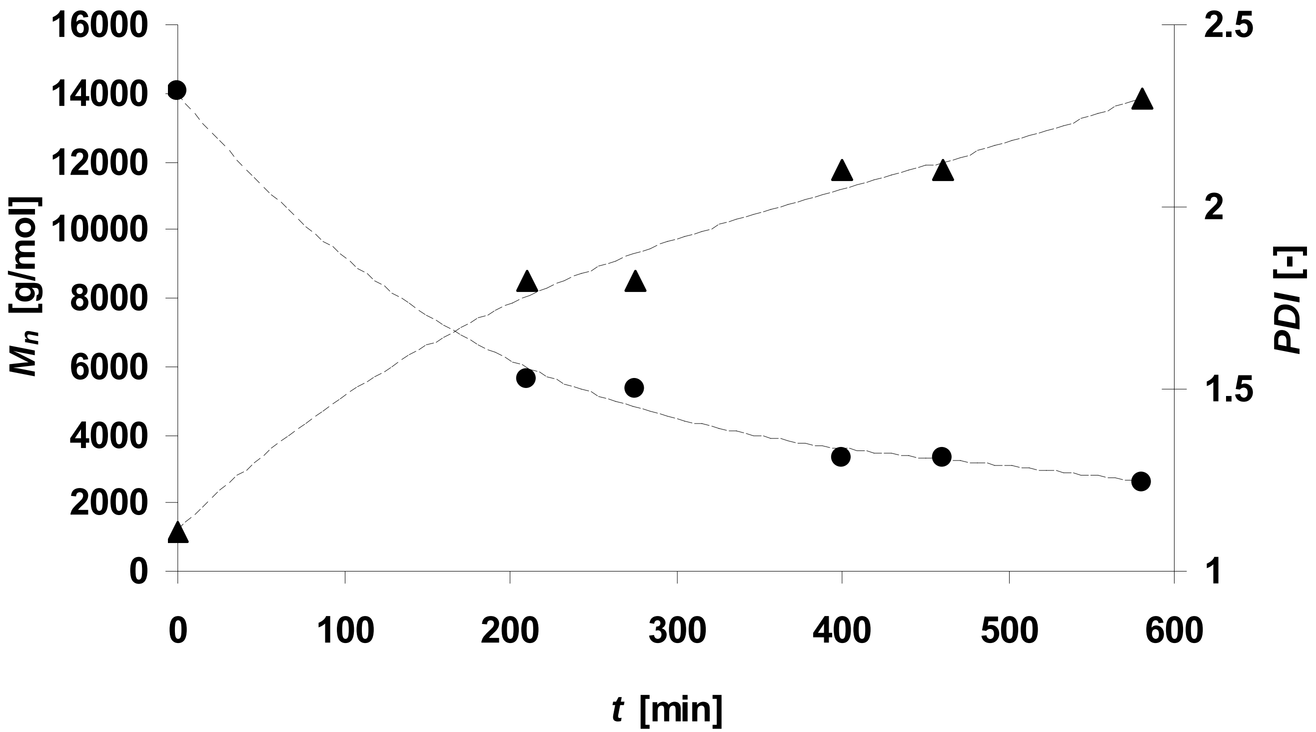
Too brittle for engineering plastic applications,
but
low molar mass PCHC might be suitable for coatings
→ controlled breakdown
(Tg high enough for powder coating applications)

Controlled breakdown of high MW PCHC

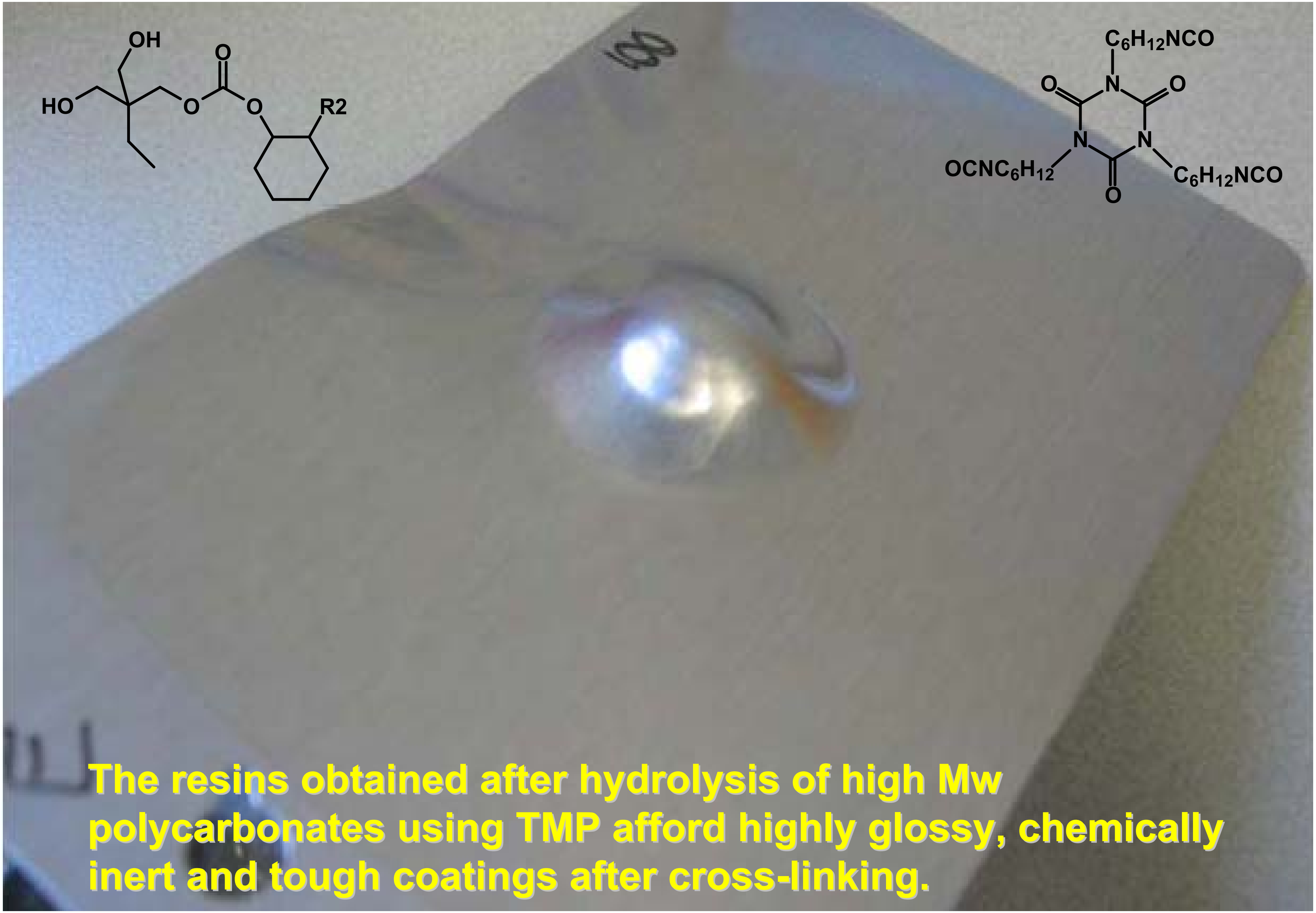


TMP-mediated break-down of high MW PCHC through alcoholysis affords OH-functional polycarbonate, curable with trifunctional isocyanate (*glycerol* also possible). R1 and R2 are polymer chain fragments.

Controlled degradation of high MW PCHC with TMP



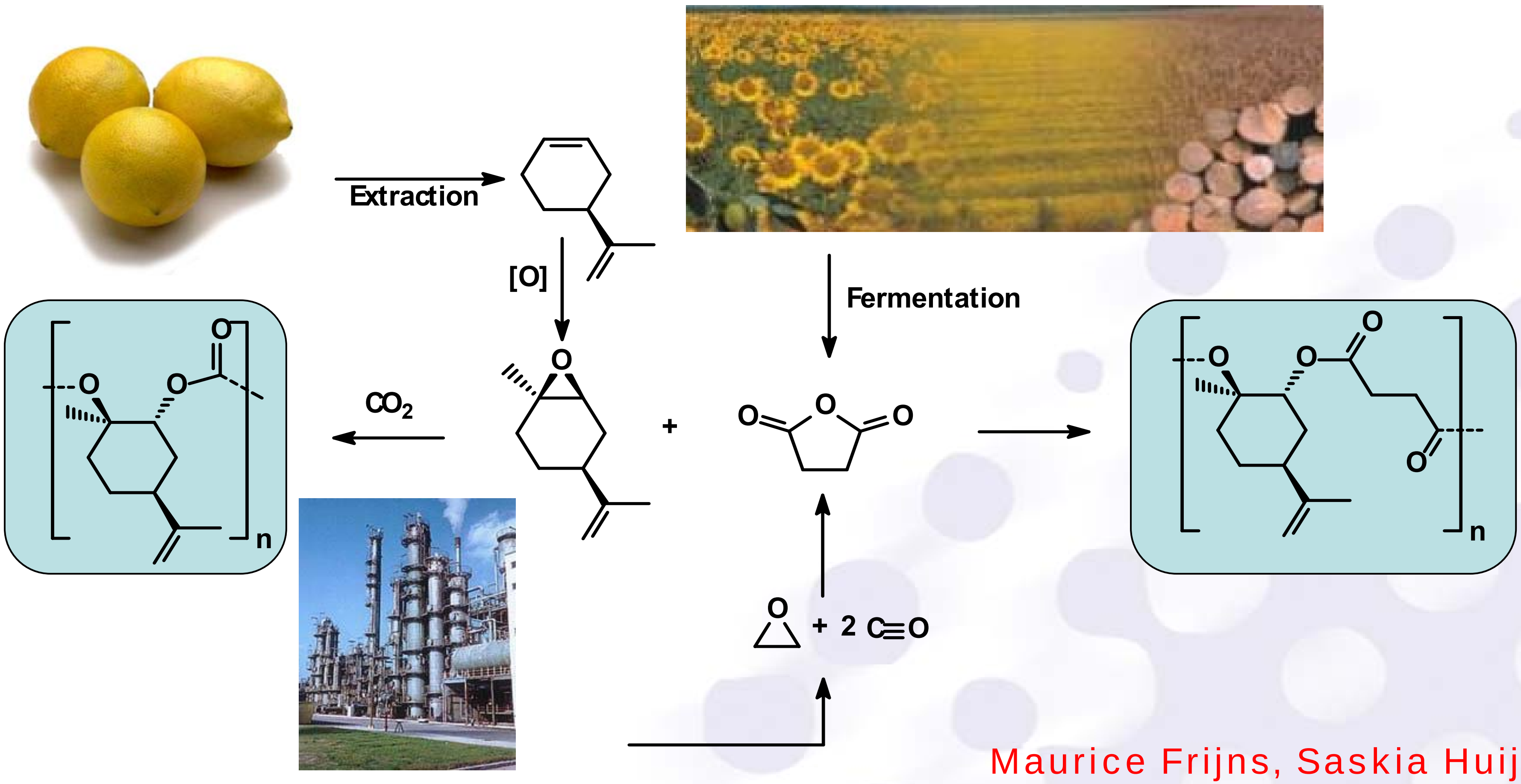
This works, but:
Preferred route: chain transfer agents furnishing OH end groups in living polymerization



The resins obtained after hydrolysis of high Mw polycarbonates using TMP afford highly glossy, chemically inert and tough coatings after cross-linking.

Catalytic routes to renewable (biodegradable) polymers

An example of fully renewable, biodegradable polymers.



Maurice Frijns, Saskia Huijser

C.M. Byrne et al, J. Am. Chem. Soc., 126, 11404-11405 (2004)

One of the components of the air is a promising raw material for the manufacturing of novel, high performance coating materials

One of the components of the air is a promising raw material for the manufacturing of novel, high performance coating materials

But we cannot solve the 'greenhouse' problem by polymerizing all carbon dioxide present in the air !

All four examples illustrate DPI 'chain-of-knowledge' philosophy and have a flavor of important aspects of DPI's future strategy

- **Sustainability**

  Where possible use biomass as feedstock

  Enhance lifetime by e.g. enhancing coatings UV stability
- **Alternative (bio)catalytic routes to existing bulk and new specialty polymers. Full understanding of catalysis mechanisms is required. Join forces with modelling groups**
- **Upgrade existing polymers with 'smart additives'**
- **Environment deserves priority #1**

  Cleaner processes (in water or carbon dioxide). More focus on process development is required.

  Compostable, CO_2-neutral polymers

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The elements help making the DPI dream to come true

- **Natural resources for new polymers**
- **Biocatalysts from nature furnishing new materials**
- **‘Greenhouse’ gas from the air as feedstock for new polymers**
- **Water as an environmentally benign medium for the manufacturing of nanocomposites**
- **Fire (heat) for taking the chemistry ‘over the top’**

DPI, congratulations with your 10th anniversary !

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