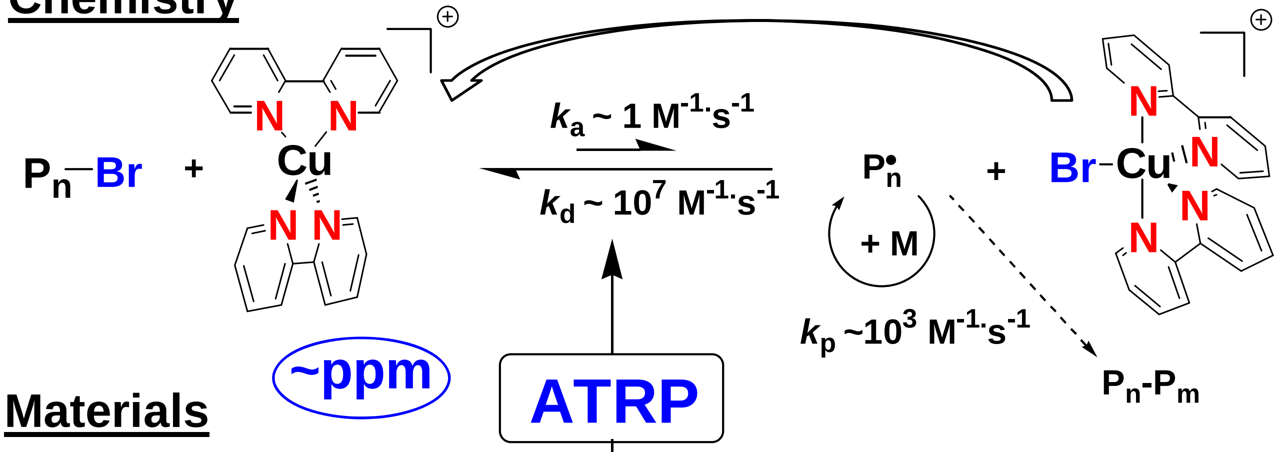
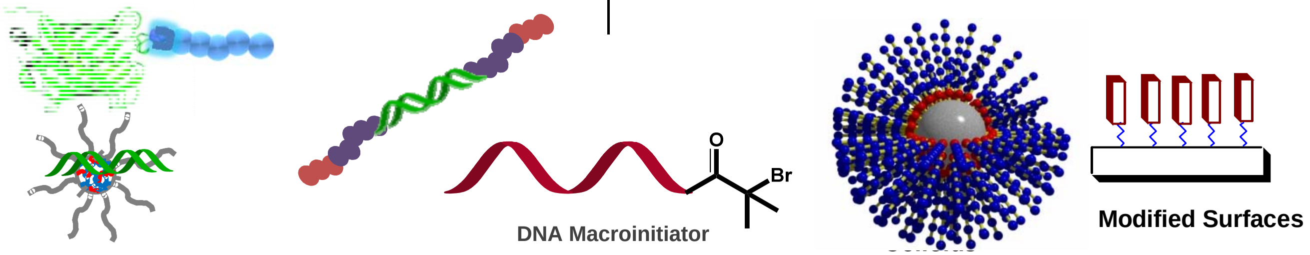
# Macromolecular Engineering
## by Taming Free Radicals

**Chemistry**



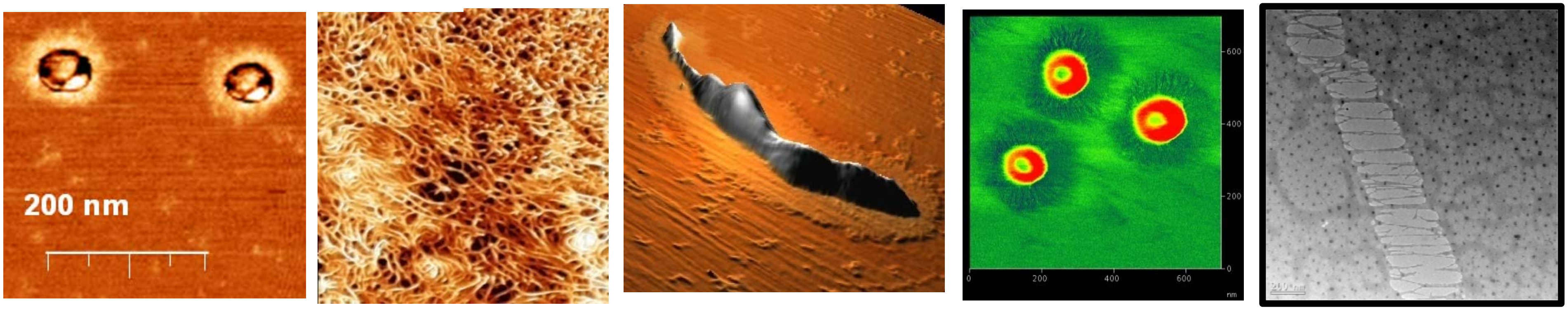
**Materials**



Cu-mediated redox process:
-1,000,000,000 times increased activity (=> ppm Cu & environmentally benign reducing agents: Vitamin C, sugars, iron, electrical current, light)
-Solventless or water based media

Nanostructured materials:
-controlled complex architecture
-hybrids and bioconjugates

Applications (16 industrial licenses):
-coatings, adhesives ,surfactants, additives, dispersants, lubricants, gels, thermoplastic elastomers, sealants, health & beauty products, nanocomposites, hybrids, electronics, biomaterials…



**60 members ATRP/CRP Consortia** *Aculon, Akzo, Arkema, Asahi, Asahi Medical, Atofina, ATRP Solutions, Bayer, BFGoodrich, Biohybrid Solutions, Boston Scientific, BYK, Cabot, Ciba, Ciba Vision, CIP, Dainippon Ink, Degussa, DIC, Dionex, DSM, Elf, Encapson, Entegris, Evonik, GE, Geon, GIRSA, Henkel, HTIG, JSR, Kaneka, Kilimanjaro Energy, Kuraray, LG Chem, Lion, Merck, Mitsubishi, Mitsui, Motorola, 3M, Nalco, Nanoderm, Nippon Goshei, Nitto Denko, PPG, Roehner, Rohm & Haas, Rohmax,Sasol, Seeo, Foshan Sheen Sun, Silberline, Sinopec, Syngenta, Solvay, Teijin, ThermoFisher, WEP & Zeon.*

Carnegie Mellon University

# Atom Transfer Radical Addition

$h\nu$

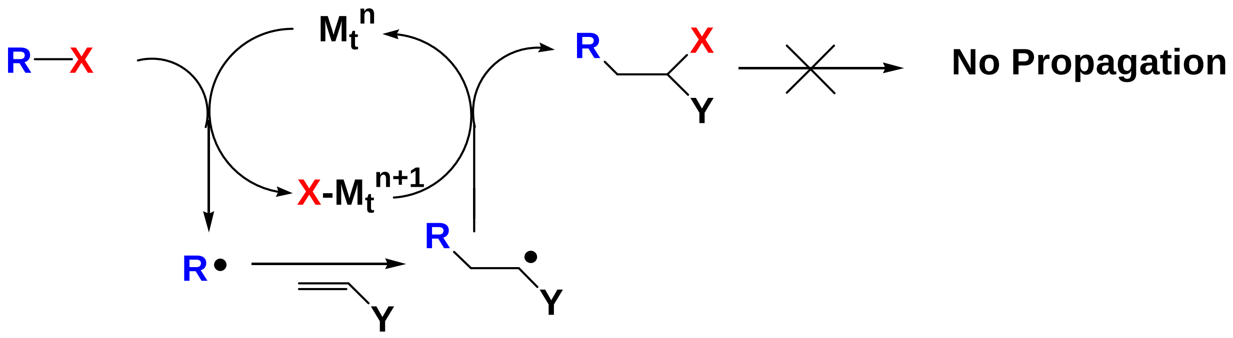
$H\text{--}CCl_3$

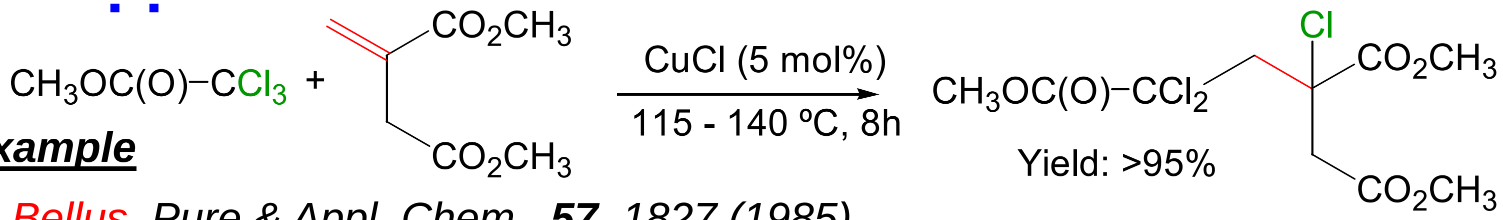
Kharasch, *1940'*

Minisci, *1961*

$Cl\text{--}CHCl_2$

**??**





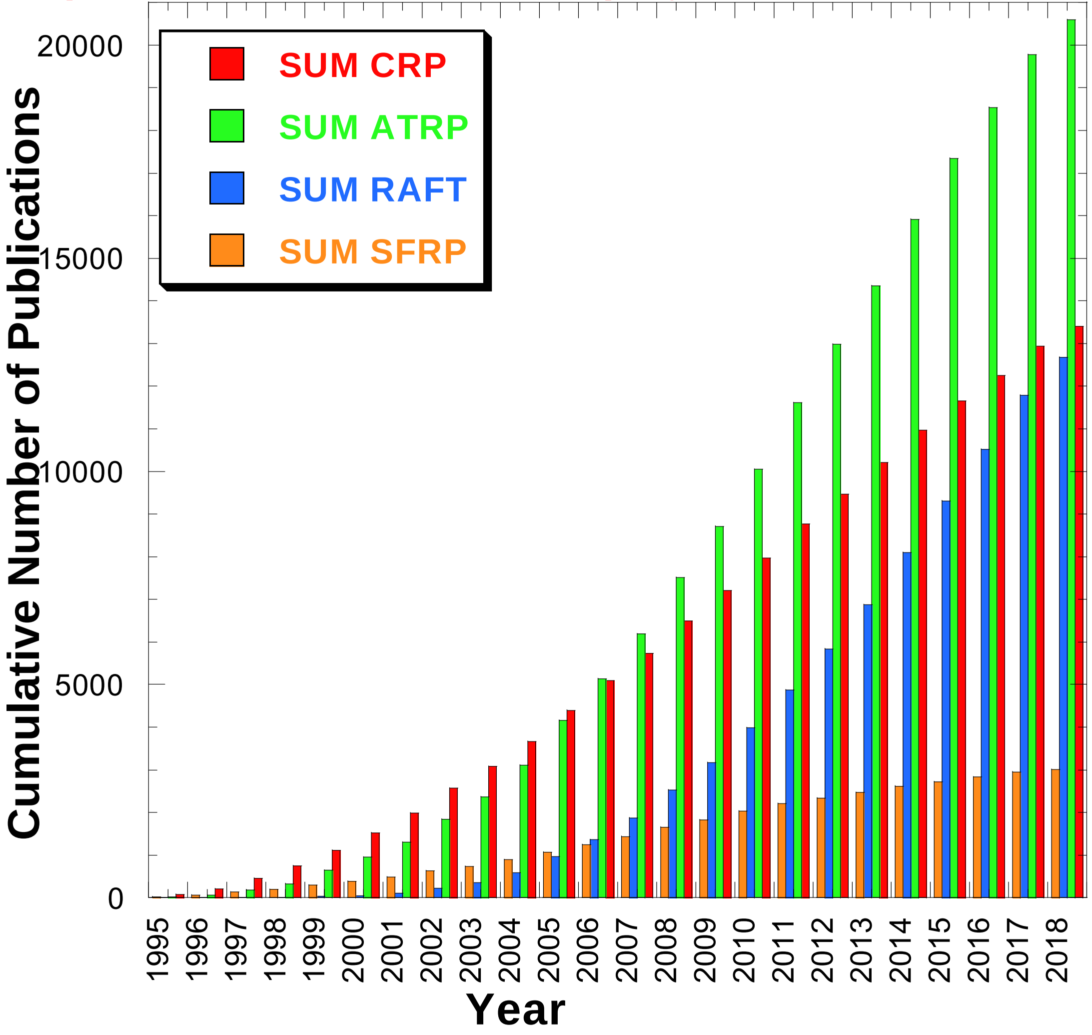
***Example***

*D. Bellus, Pure & Appl. Chem.*, ***57***, *1827 (1985)*

# Reversible-Deactivation Radical Polymerization

- **Conventional Free Radical Polymerization: ~ 100 M tons/year (~50% polymers)**
  - **bulk, solution, water & tolerance of functionalities**
  - ***control of polymer architecture impossible; no block, star copolymers, etc.***
- **>40,000 papers on CRP**
  - **(>20,000 ATRP since ‘95)**
  - ***Google: atrp >1,800,000***
- ***>3,000 patents on CRP***
  - ***(>2,000 ATRP since ‘95)***
- **Anticipated market for CRP:**
  - **>20$billion/year**
  - ***Bob Matheson (DuPont)***
- **Applications:**
  - **coatings, adhesives, surfactants, dispersants, lubricants, gels, additives, thermoplastic elastomers, sealants, health & beauty, hybrids, nanocomposites, electronics, biomaterials, …**

***Advanced Materials***



***SciFinder Scholar: August 25, 2018***

# Methods for Controlling Radical Polymerization

- EQUILIBRIA BETWEEN RADICALS AND DORMANT SPECIES
- **Extending** life of propagating chains (from <1s to >1 h)
- **Quantitative initiation** (from $R_i$~$R_t$<<$R_p$ to $R_i$»$R_p$>>$R_t$)

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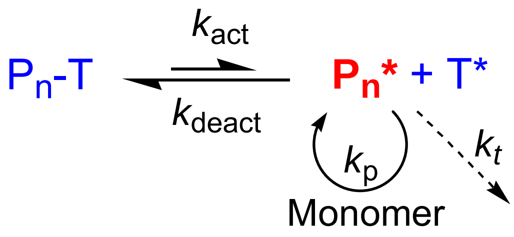
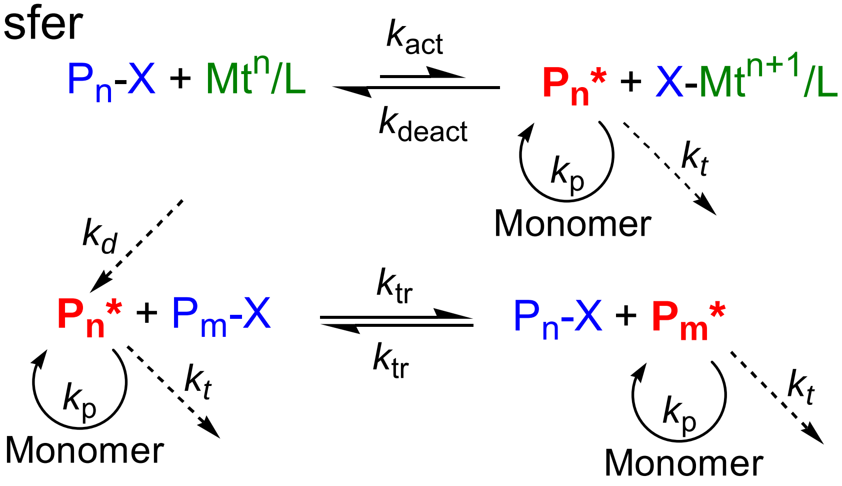
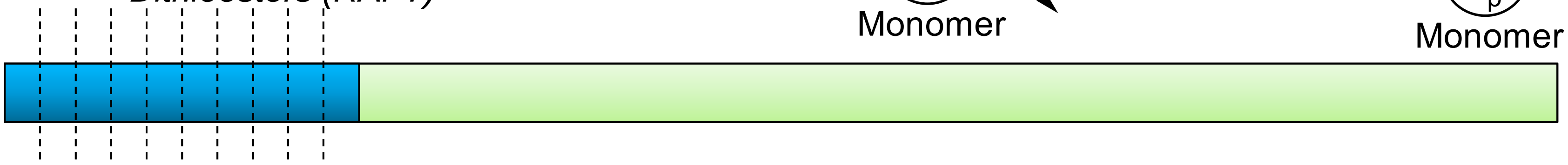
- Reversible deactivation by coupling (SFRP)
  - Nitroxide-mediated polymerization



- Catalytic reversible deactivation by atom transfer
  - ATRP
- Degenerative transfer
  - *Atom or group transfer (I, Te, Bi,…)*
  - *Addition-Fragmentation:*
    - *Dithioesters (RAFT)*





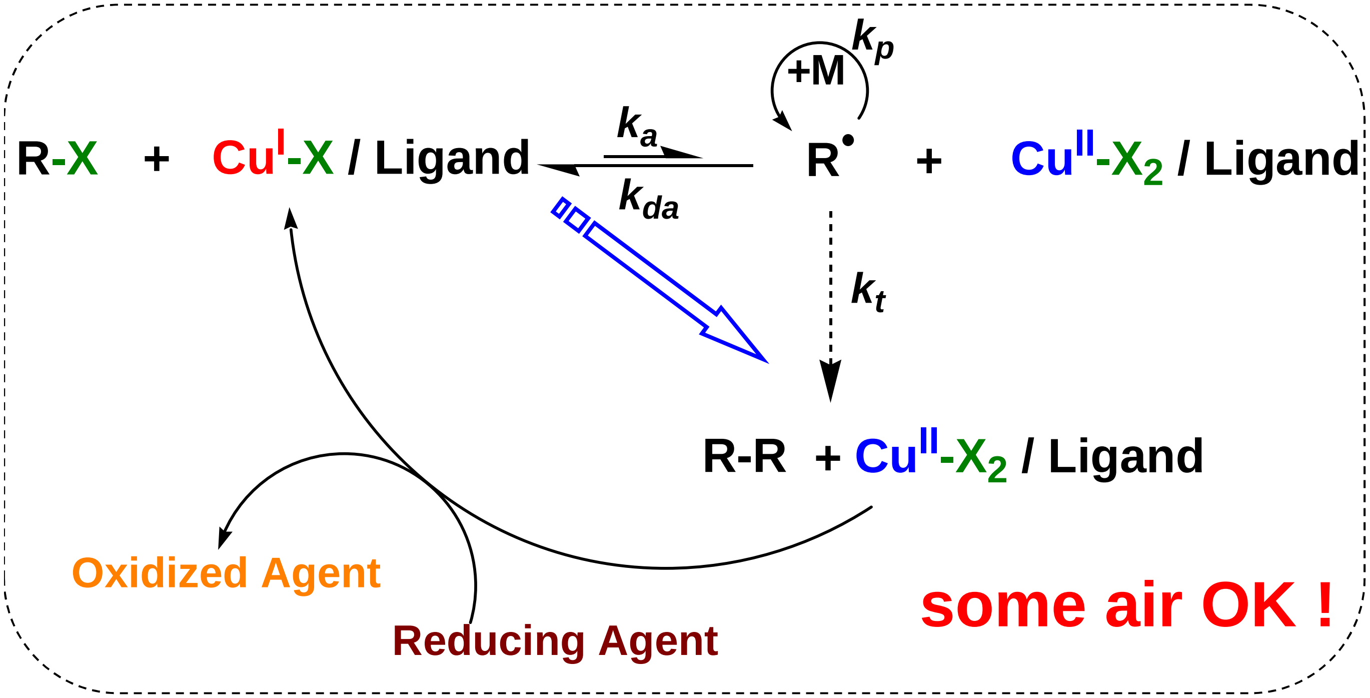
**1 s** radical lifetime
1000 × **1 ms** = 1 s

1000 × **1 ms** + 1000 × **1 min** ≈ **1 day**

*Carnegie Mellon University*

# ATRP with ppm Cu

**Traditional ATRP: [Cu] >1,000 ppm => Now: [Cu]<50 ppm**



$$R\text{-}X + Cu^{I}\text{-}X / Ligand \underset{k_{da}}{\overset{k_a}{\rightleftharpoons}} R^{\bullet} + Cu^{II}\text{-}X_2 / Ligand$$

+M $k_p$

$k_t$

R-R + $Cu^{II}\text{-}X_2$ / Ligand

Oxidized Agent

Reducing Agent

**some air OK !**

$$\overset{(II)}{Sn(EH)_2} + \overset{(II)}{2CuCl_2/Ligand} \overset{K_{eq}}{\rightleftharpoons} \overset{(IV)}{Sn(EH)_2Cl_2} + \overset{(I)}{2CuCl/Ligand}$$

$$Cu(0) + L + CuCl_2/Ligand \rightleftharpoons 2CuCl/Ligand$$

$$AIBN + 2CuCl_2/Ligand \longrightarrow 2Me_2C(CN)\text{-}Cl + 2CuCl/Ligand$$

$K_{eq}$: $Me_6TREN$<PMDETA<bipy & **phenol< sugar<amine<hydrazine<asc. Acid**
**also Fe<Mg<Zn**

Jakubowski, W.; Min, K.; Matyjaszewski, K. *Macromolecules* **2006**, 39

Matyjaszewski, K. et al., *Angew. Chem.* **2006**, 4482, *PNAS*, **2006**, 15309, *Macromolecules* **2013,** 8749

**2000 ppm of Cu(I)**

| St | Ini | CuCl | dNbpy |
|---|---|---|---|
| 500 | 1 | 1 | 2 |

**200 ppm of Cu(I)**

| St | Ini | CuCl | dNbpy |
|---|---|---|---|
| 500 | 1 | 0.1 | 0.2 |

**20 ppm of Cu(I)**

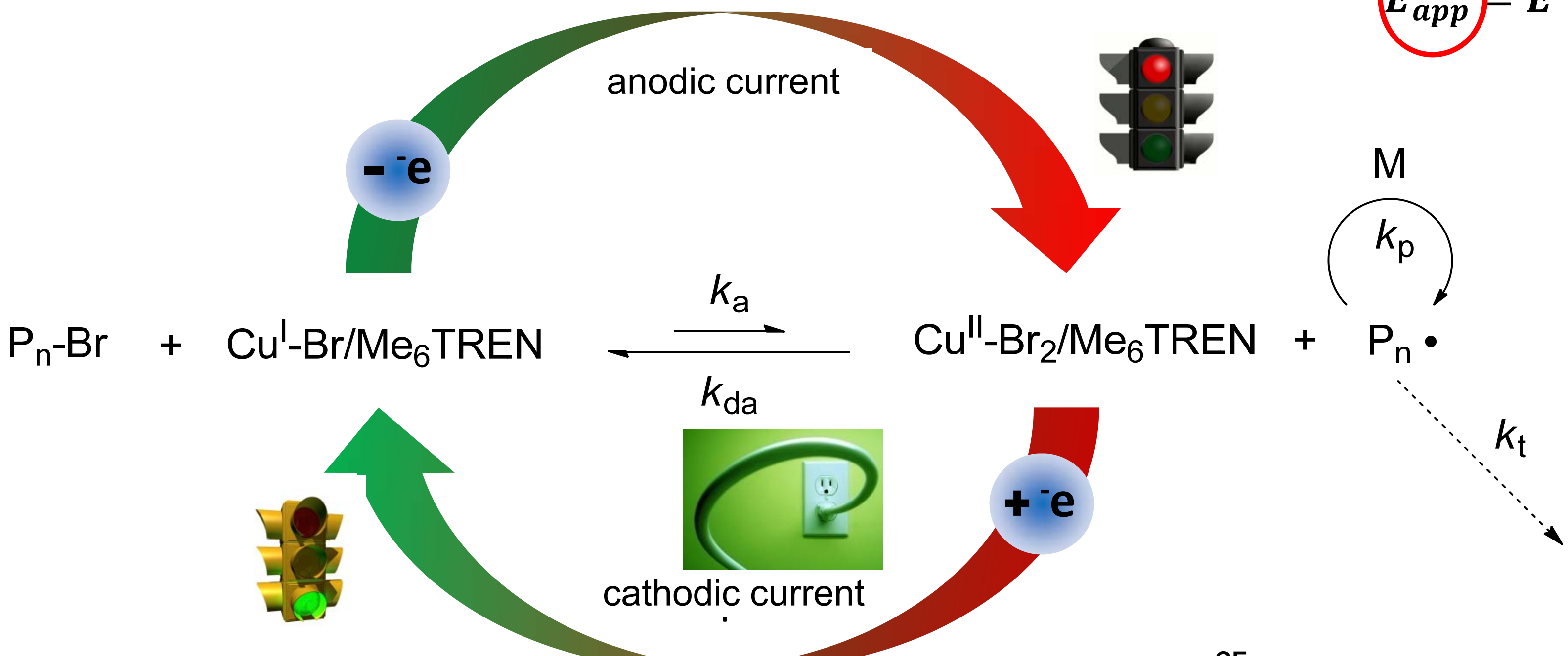
| St | Ini | CuCl | dNbpy |
|---|---|---|---|
| 500 | 1 | 0.01 | 0.02 |

# *e*-ATRP

## *Activators Mediated by Potential ATRP*

**Nernst Equation:**

$$E_{app} = E^{\circ} - \frac{RT}{zF} ln \frac{[Cu^{I}]}{[Cu^{II}]}$$

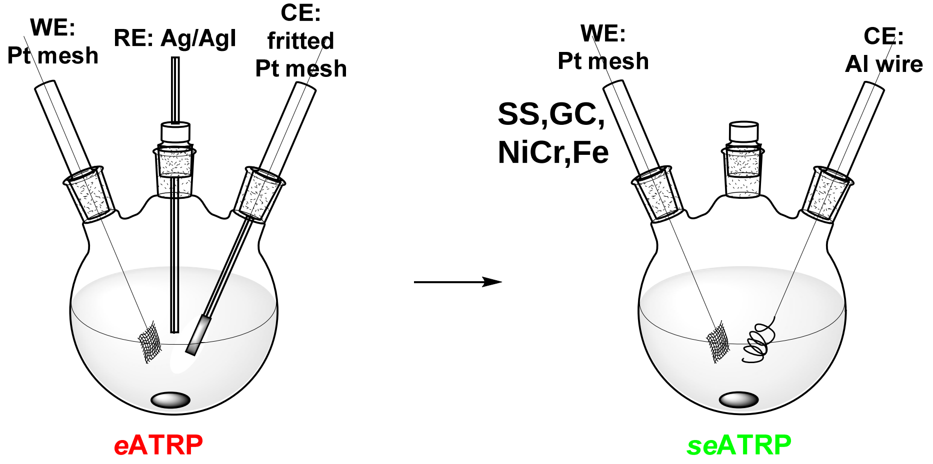


$$P_n\text{-Br} + Cu^{I}\text{-Br/Me}_6\text{TREN} \underset{k_{da}}{\overset{k_a}{\rightleftharpoons}} Cu^{II}\text{-Br}_2\text{/Me}_6\text{TREN} + P_n\bullet$$

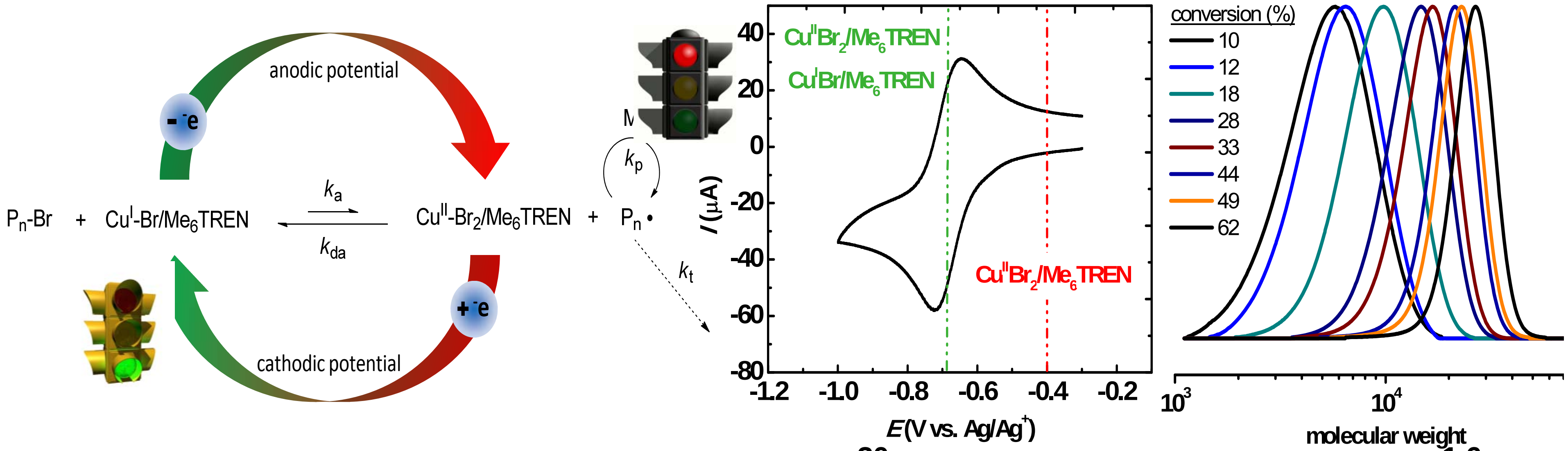
**Potential of Electrochemistry**

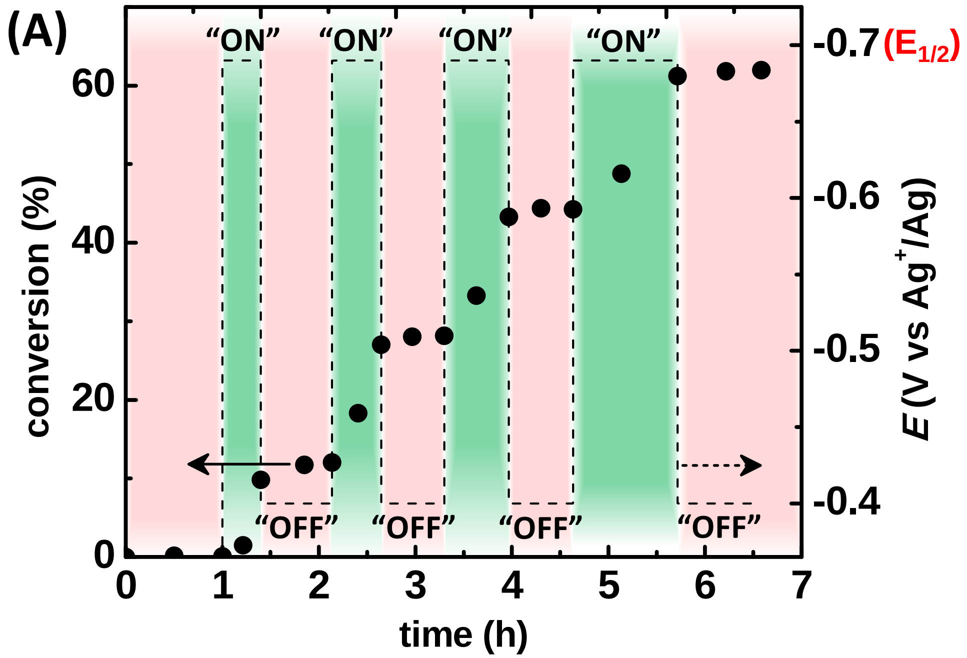
- Additional control (Q, E, I)
- No chemical reducing agents
- Tolerance to $O_2$
- Simplified purification (electrodeposition)

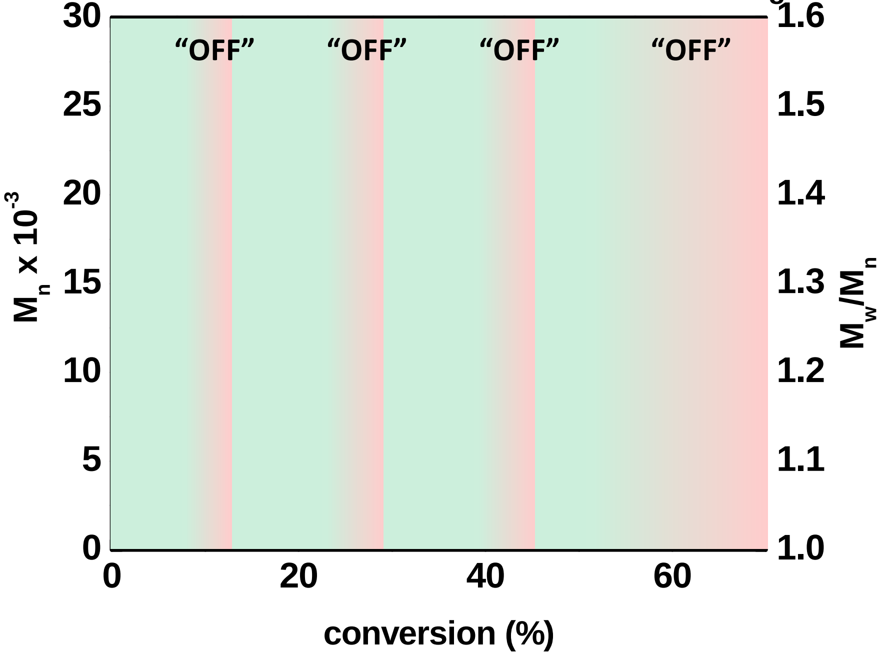
*Science*, 332, 81 (**2011**)



# Electrochemically Controlled ATRP

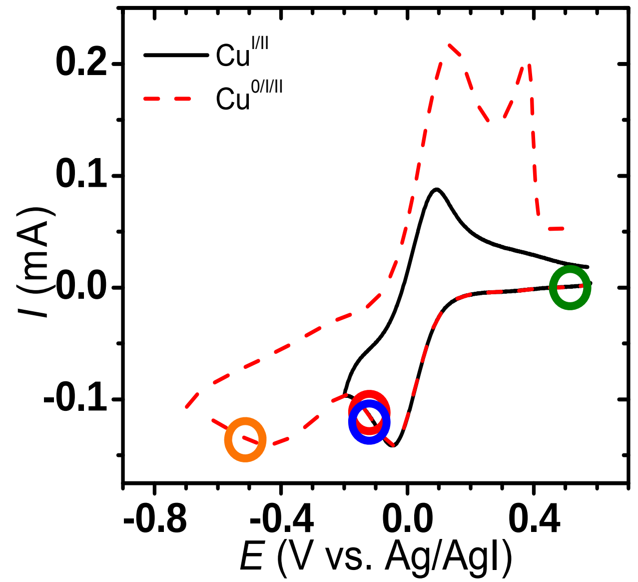




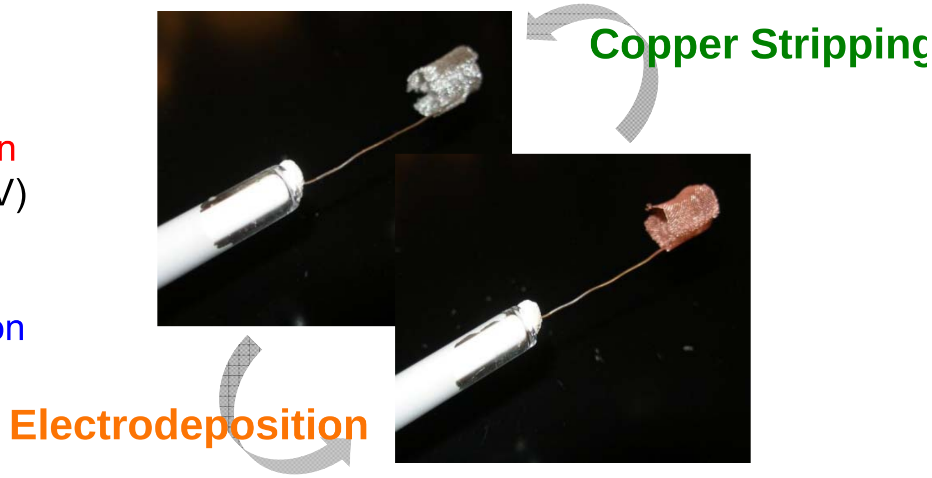


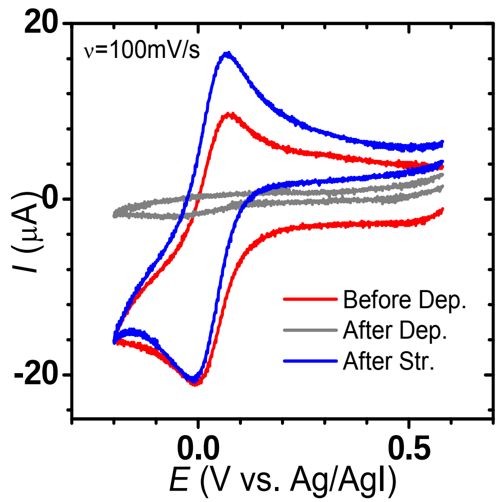
**[MA]/[EBP]/[Me$_6$TREN]/[Cu$^{II}$Br$_2$] = 500/1/0.2/0.2 (50 ppm); 50% MeCN at R.T.**

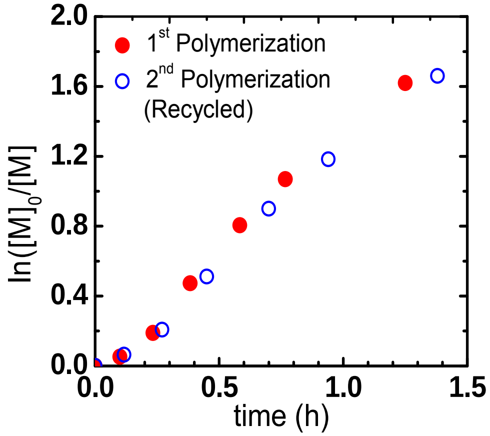
# Cu Recycling

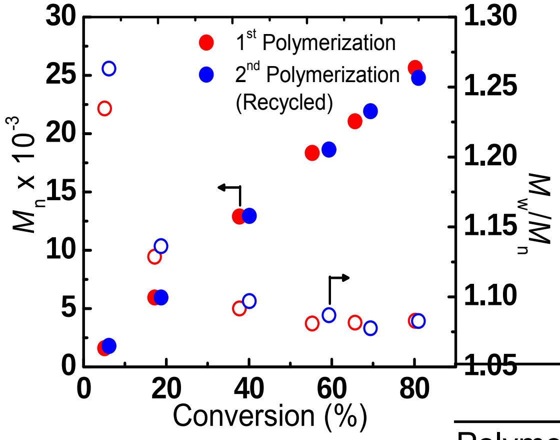


1. 1st Polymerization ($E_{app}$=$E_{pc}$-135 mV)
2. Deposition
3. Stripping
4. 2nd Polymerization







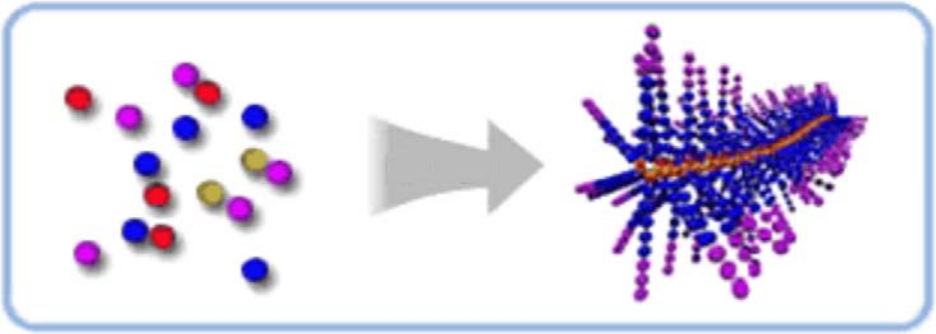


[BA]/[EBiB]/[TPMA]/[$Cu^{II}$] = 300/1/0.09/0.09, [$TBAClO_4$] = 0.2M [BA] = 3.9 M in DMF, T = 44 °C

| | **Time (h)** | **[Cu] (mM)** |
|---|---|---|
| Polymerization | 1.5 | 1.18 |
| Deposition | 8 | 0.05 (10ppm, **>98% removal**) |
| Copper stripping | 2.8 | 1.07 (**>90% recovery**) |

*Macromolecules*, **2013**, *46*, 4346–4353

# Switchable Catalysis in ATRP



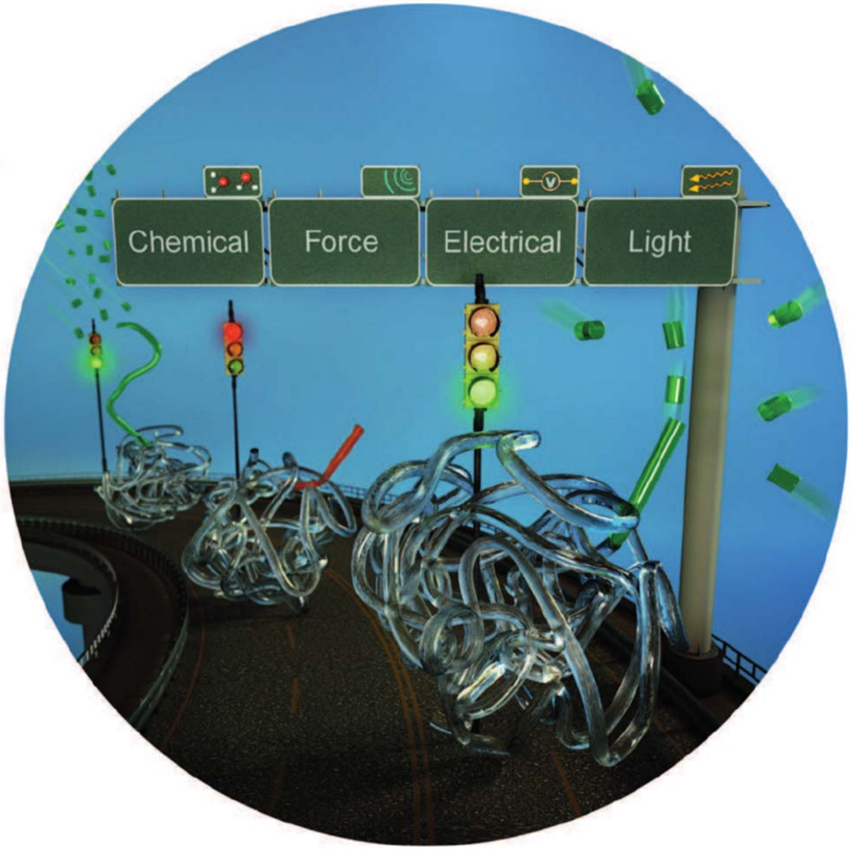
Temporal control

Spatial control

Selectivity modulation

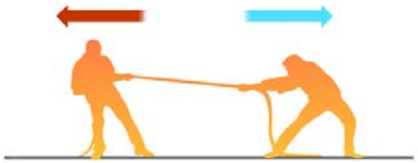
Advanced material

+



**Electrochemical**

**Photochemical**

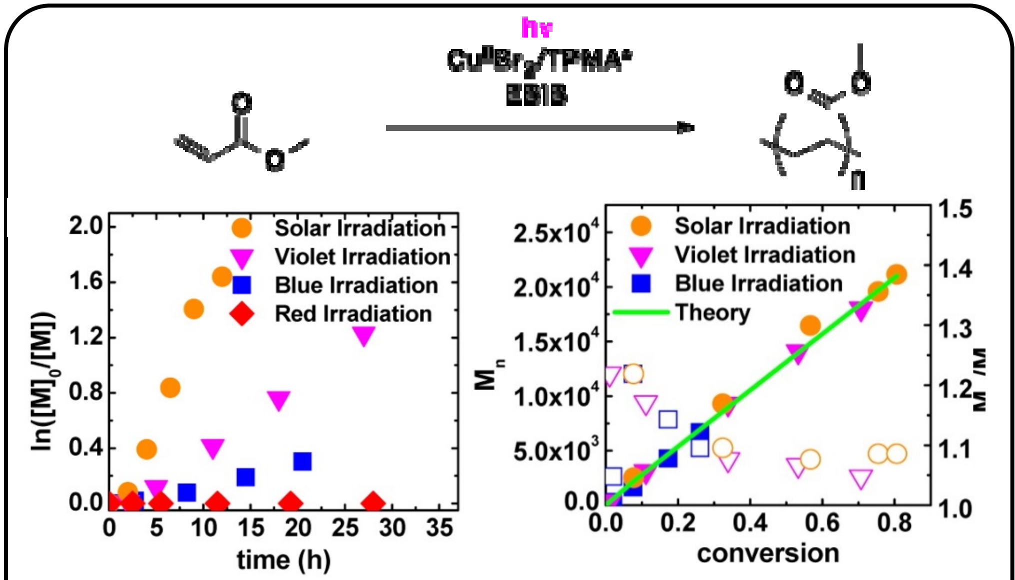


**Mechanochemical**

**Chemical**

Bielawski, C. W. et al., *Chem. Rev.*, **2016**, *116*, 1969–1992; Hawker, C. J. et al., *Angew. Chem. Int. Ed.* **2012**, 51, 2–14.

# PhotoATRP of MA with 100 ppm Cu



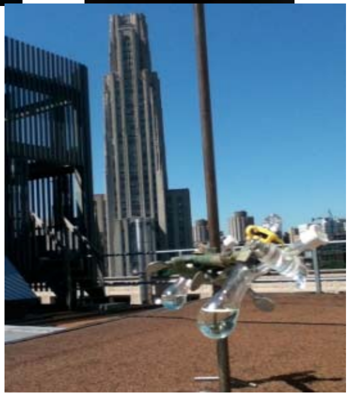
$[M]_0:[I]_0:[CuBr_2]_0:[L]_0$ = 300:1:0.03:0.135, [M] = 4.7 M in DMF

Violet

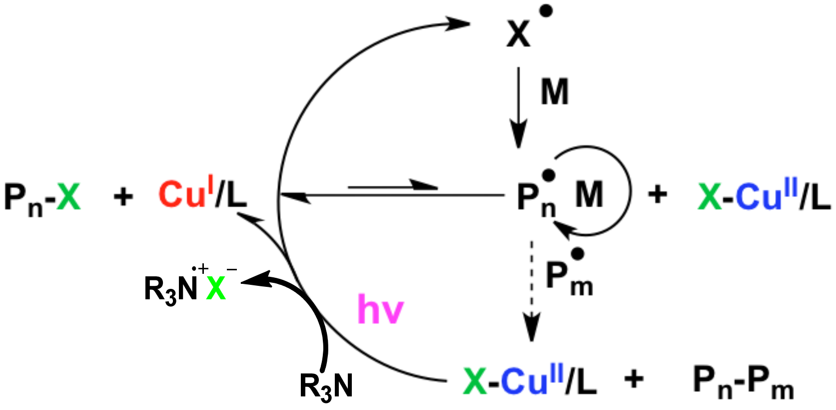
Blue

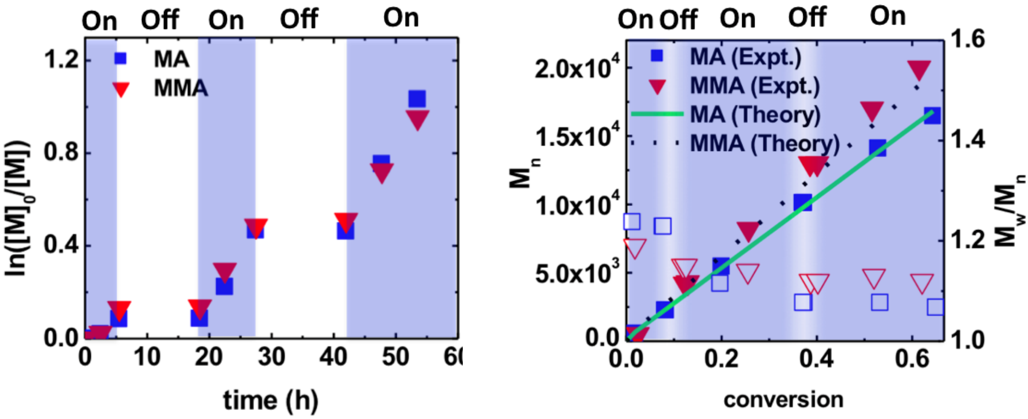
Red

Sunlight



## Proposed Mechanism

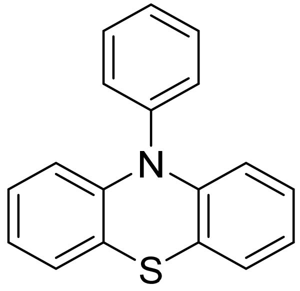




$[M]_0:[I]_0:[CuBr_2]_0:[L]_0$ = 300:1:0.03:0.135, [M] = 4.7/5.5 M in DMF, 392 nm hv

Matyjaszewski, K. et al. *ACS Macro Lett.* **2012**, 1, 1219.
Matyjaszewski, K. et al. *J. Am. Chem. Soc.* **2014**, 136, 13303.

# Photoinduced Metal-Free ATRP

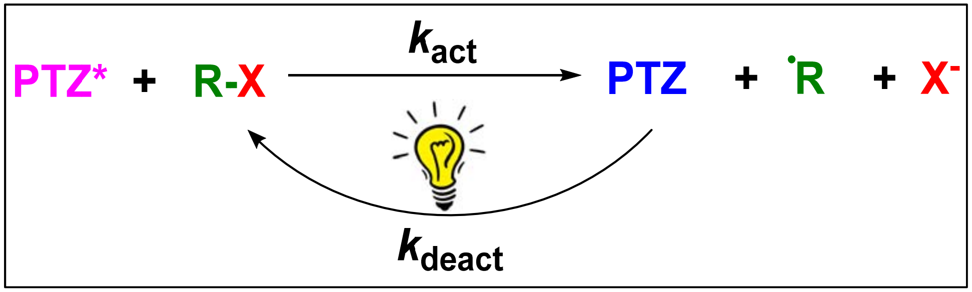


**Ph-PTZ**

$E^{red}$ = - 2.10 V vs SCE

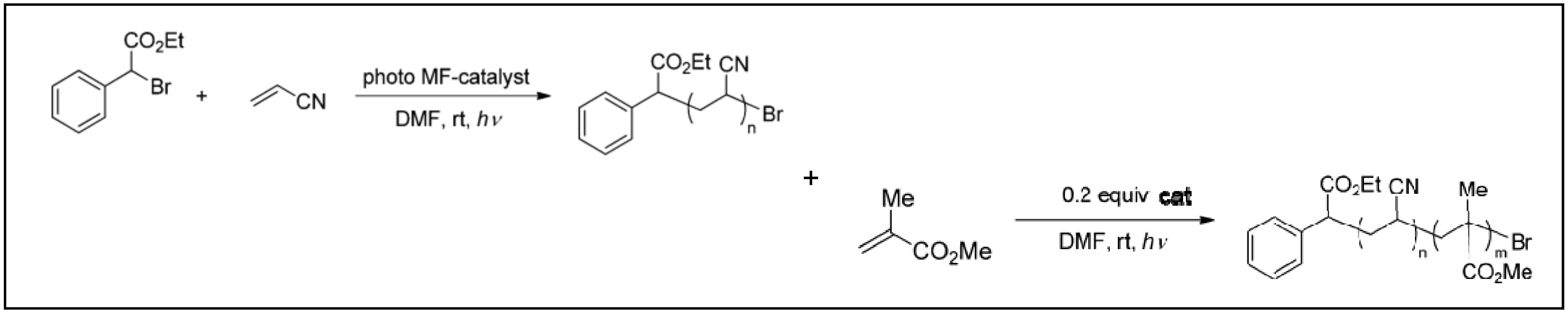
$E^{ox}$ = 0.68 V vs SCE

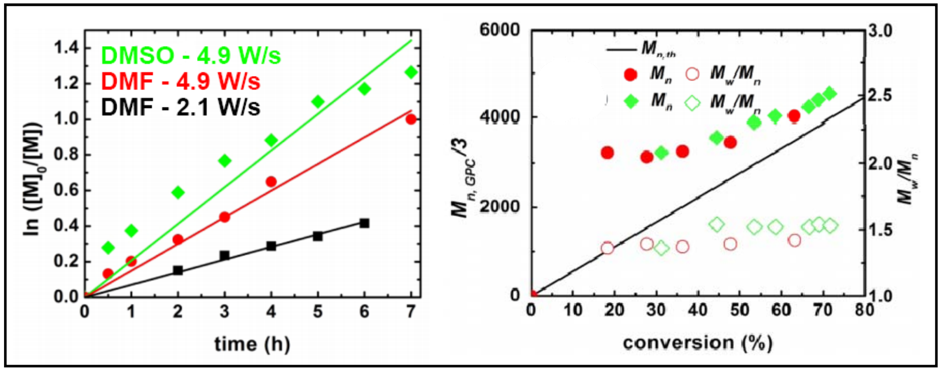
*TPMA: $E^{red}$ = - 0.3 V vs SCE*

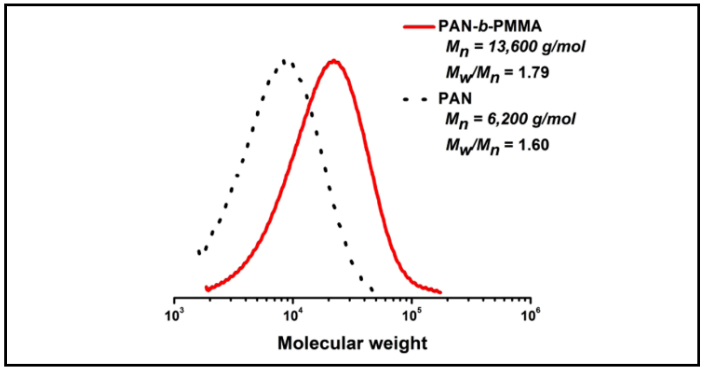


**PTZ*** + **R-X** $\xrightarrow{k_{act}}$ **PTZ** + **$^{\bullet}$R** + **$X^-$**

$k_{deact}$





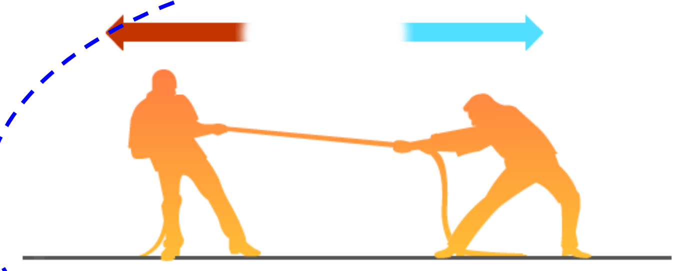


Pan, X.; Lamson, M.; Yan, J.; Matyjaszewski, K. *ACS Macro Lett.* **2015**, 192.

# Controlled Polymerization by External Spatio-temporal Regulation

**Electrochemical** Control

- eATRP
- Bipolar electrode



**Mechanochemical** Control

- Piezoelectric ATRP
- ROMP

**Chemical** Control (redox, pH)

- ARGET ATRP
- ROMP
- ROP

**Photochemical** Control

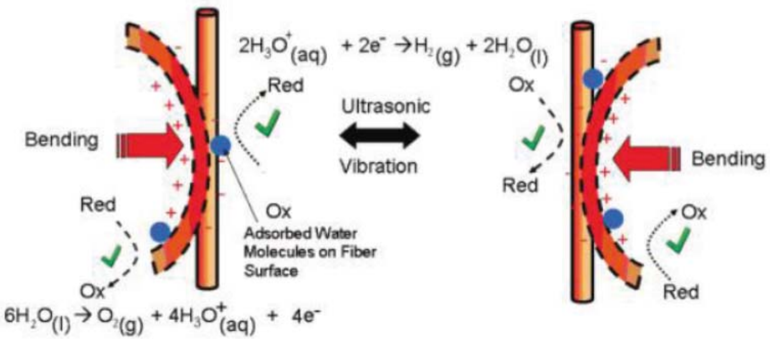
- PhotoATRP
- PET-RAFT
- NMP
- Metal-free ROMP

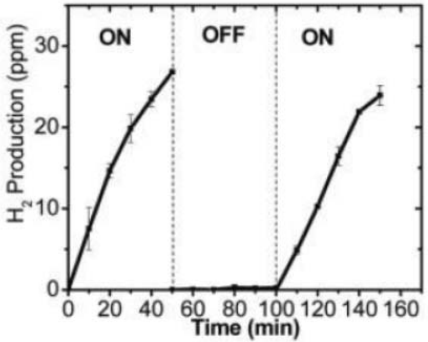
**Pressure** Control

- High-pressure ATRP
- Ethylene coordination polymerization

# MechanoATRP: Background

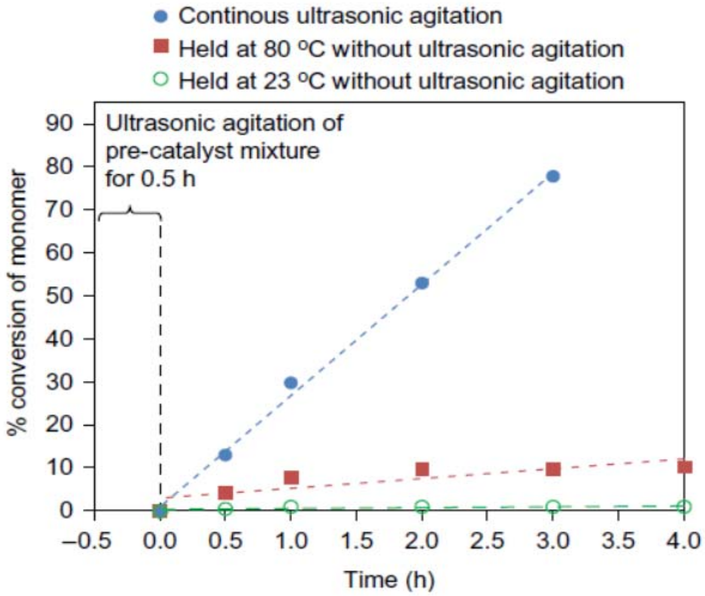
## Ultrasound-induced water splitting in the presence $BaTiO_3$





**Piezoelectric Potential > 1.23 V**

## Mechanically controlled ATRP in the presence of $BaTiO_3$

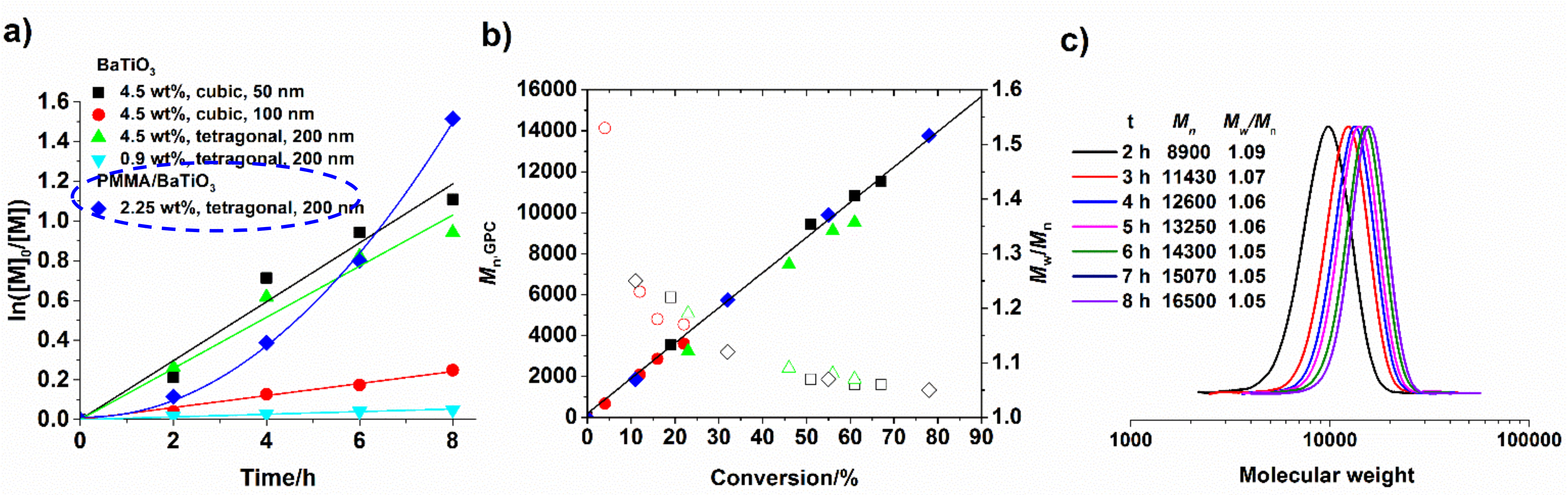


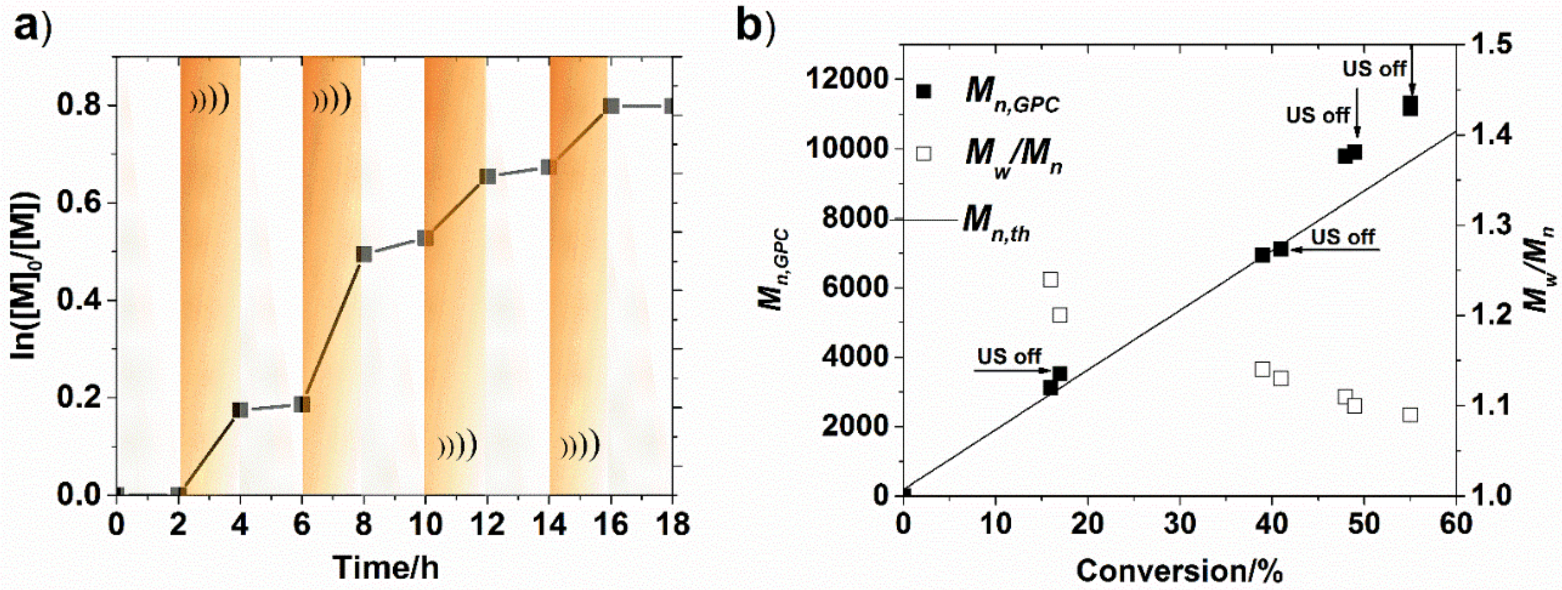
- **High concentration of catalyst (10 000 ppm)**
- **Low molecular weight $M_n$< 3000**
- **No temporal control**

[Cu(OTf)2]:[Me6TREN]:[Bu4NBr]:[EBiB]:[BA] = 0.04:0.04:0.04:0.04:4
4.5 wt% BaTiO3

Hong, K.-S.; Xu, H.; Konishi, H.; Li, X. *The Journal of Physical Chemistry Letters* **2010,** 1, (6), 997-1002.
Mohapatra, H.; Kleiman, M.; Esser-Kahn, A. P. *Nat Chem* **2017,** 135-139.

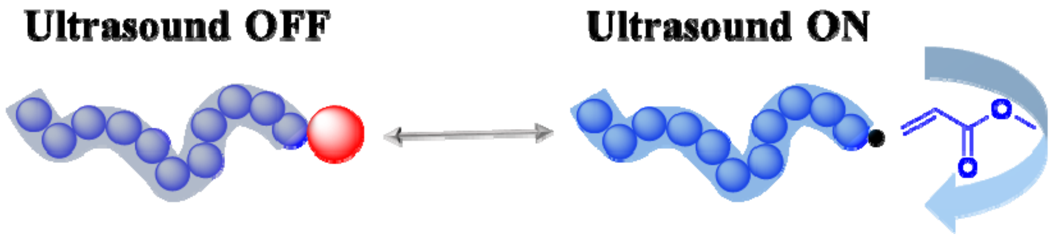
# Temporal MechanoATRP @ 100 ppm CuBr$_2$/TPMA

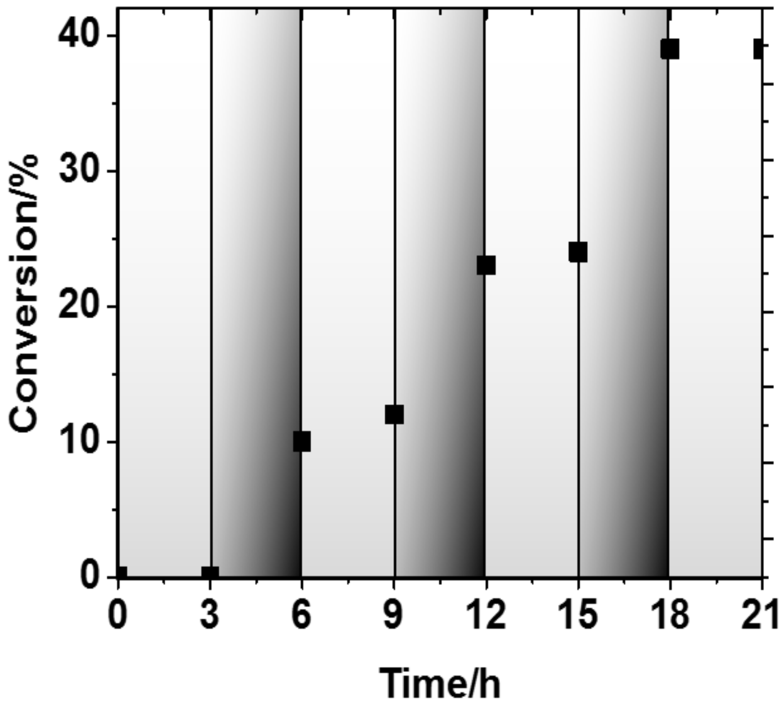


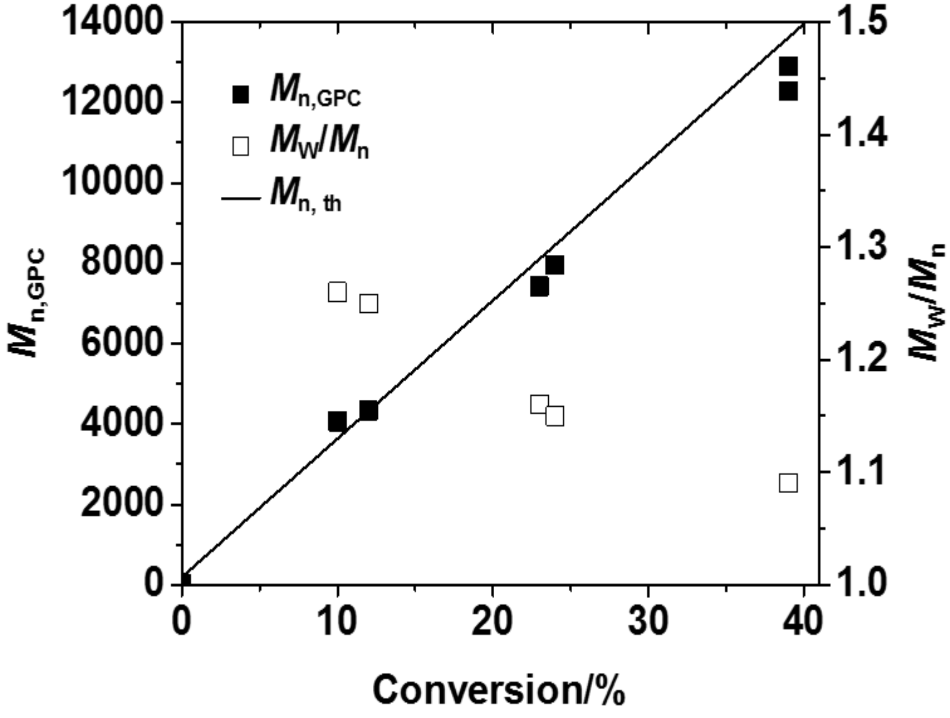


*ACS Macro Lett.* **2017**, 526

# Switchable mechanoATRP of MA with ZnO





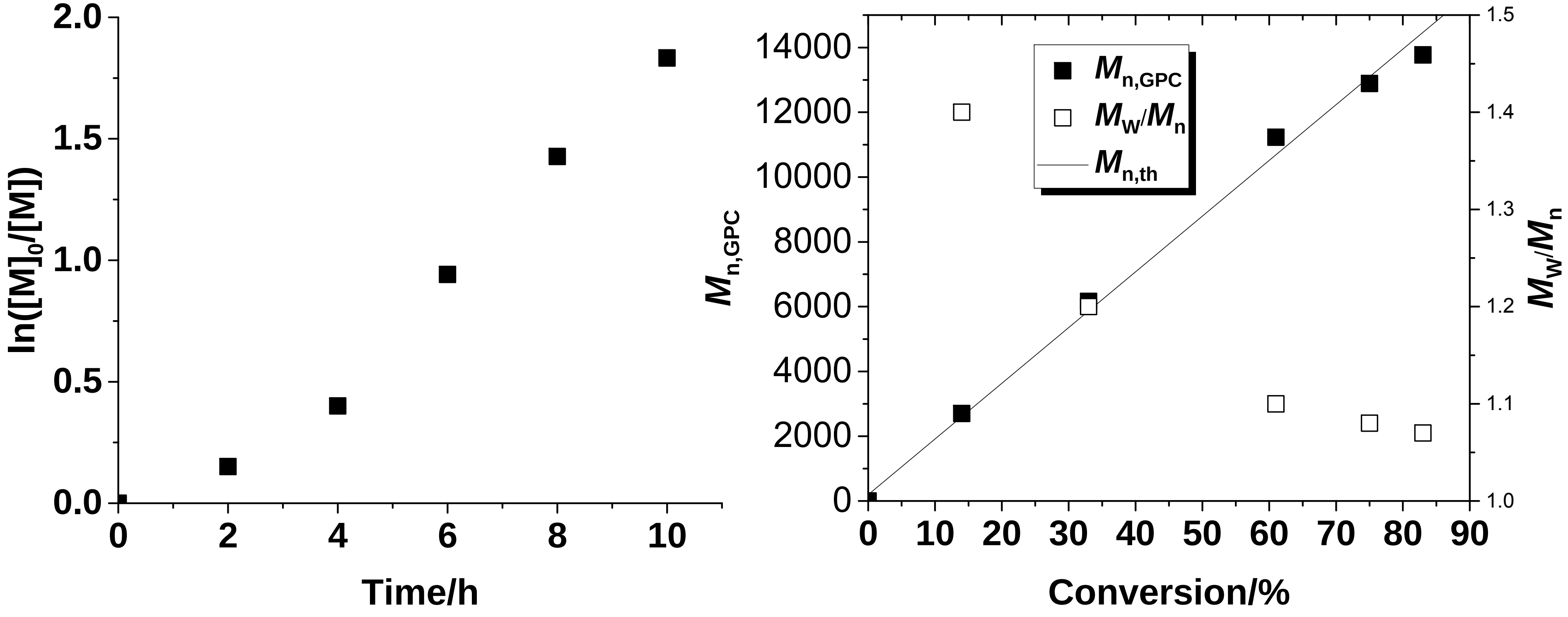


150 ppm $Cu^{II}$, 0.03 wt% 18 nm ZnO, in 50% v/v DMSO. T < 30 $^{o}$C. US bath, 40 kHz, 70 W.

- Loading 100x less than with $BaTiO_3$ (375 ppm vs 36,500 ppm)

# “Homogeneous” MechanoATRP

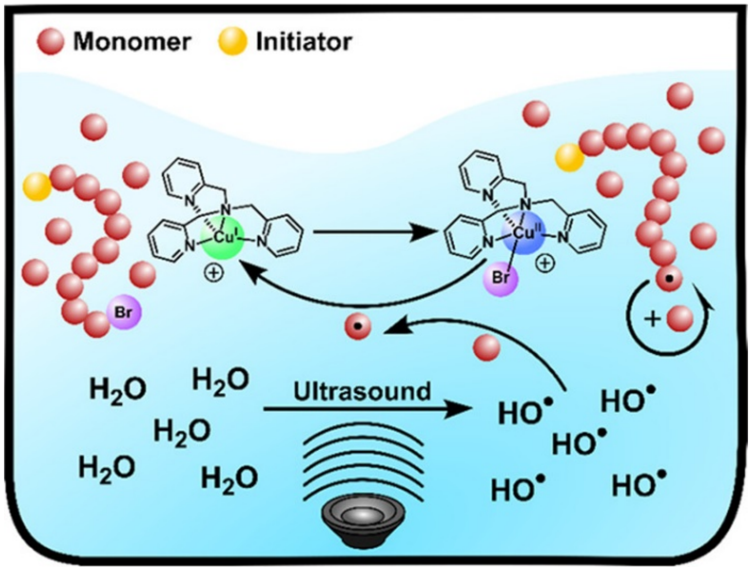
## OA-coated  5 nm ZnO

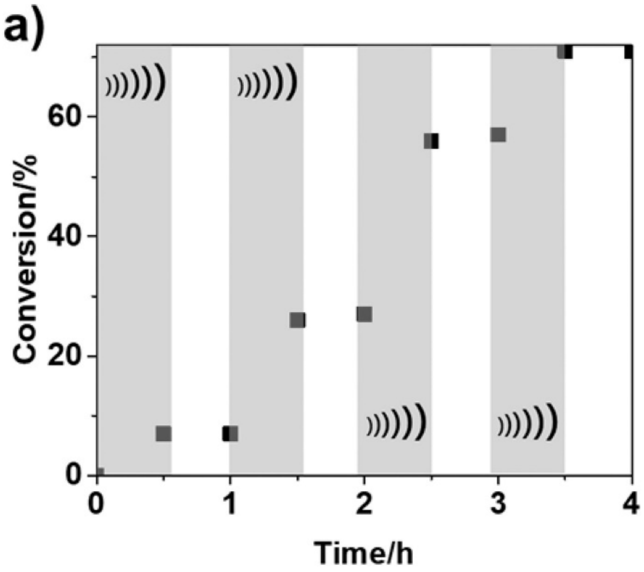


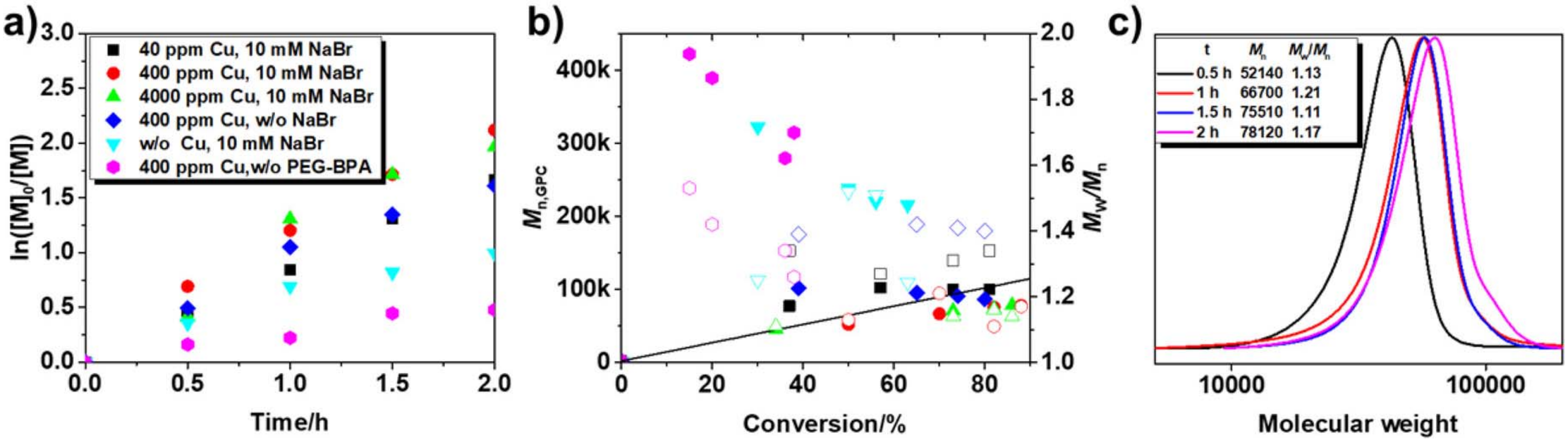
**$[MA]_0$:$[EBiB]_0$:$[CuBr_2]_0$:$[TPMA]_0$= 200:1:0.03:0.18:in 50% v/v DMSO,**
**0.06 wt% *(100 x less than $BaTiO_3$)* OA-ZnO (5 nm), T < 30 $^o$C.**
**US bath, 40 kHz, 70 W.**

*Control experiment: without ultrasound, 3% conversion after 8 h stirring.*

# SonoATRP in Water







Wang *et.al.*, *ACS Macro Lett.*, **2018**, *7*, 275-280

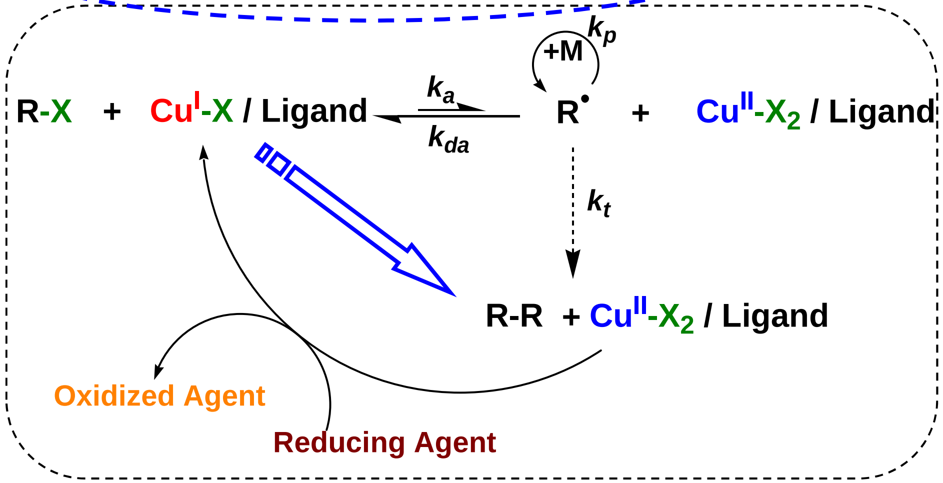
# ATRP with ppm Level of Cu
# *(stop ATRP by stopping regeneration)*

**Traditional ATRP: Cu>1,000ppm =>** **Now: Cu<20ppm**

**2000 ppm of Cu(I)**

St / Ini / CuCl / dNbpy
500 / 1 / 1 / 2

**ARGET: Activators Re-Generated by Electron Transfer**
**ICAR: Initiators for Continuous Activators Regeneration**
**SARA: Supplemental Activators & Reducing Agents**
**eATRP; photoATRP, mechanoATRP, etc,..**



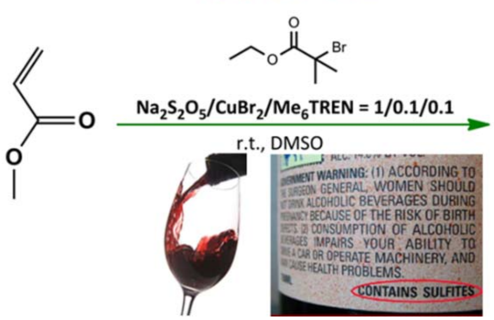
$$M_w/M_n = 1 + \frac{k_p[R-X]_o}{k_d[X-Cu(II)]}\left(\frac{2}{p}-1\right)$$

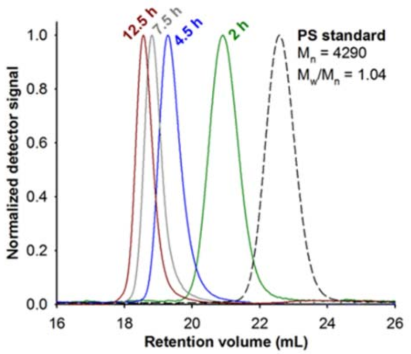
$$[X\text{-}Cu^{II}]/[Cu^{I}] = K_{ATRP}[RX]/[R^*]$$

**$K_{ATRP}$: TPMA*>$Me_6$TREN>TPMA> PMDETA>bipy**

**Rate of ATRP depends on reduction rate : phenol<sugar< <u>amine</u> (DMAEMA or L)<hydrazine < $Sn^{II}$ < asc. acid < sulfites! also Fe/Cu<Mg<Zn, Ag!**

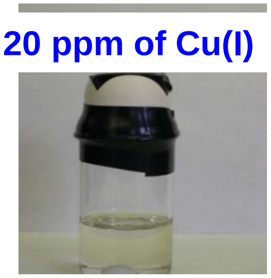
**SARA ATRP**





Matyjaszewski, K. et al., *Macromolecules* **2006**, 39; *Angew. Chem.* **2006**, 4482, *PNAS*, **2006**, 15309, *Science*, **2011**, *ACS MacroLetters* **2012, 2017**; *Macromolecules* **2013, 2015, 2017**; *JACS* **2014, 2015,2016,2017**

**20 ppm of Cu(I)**

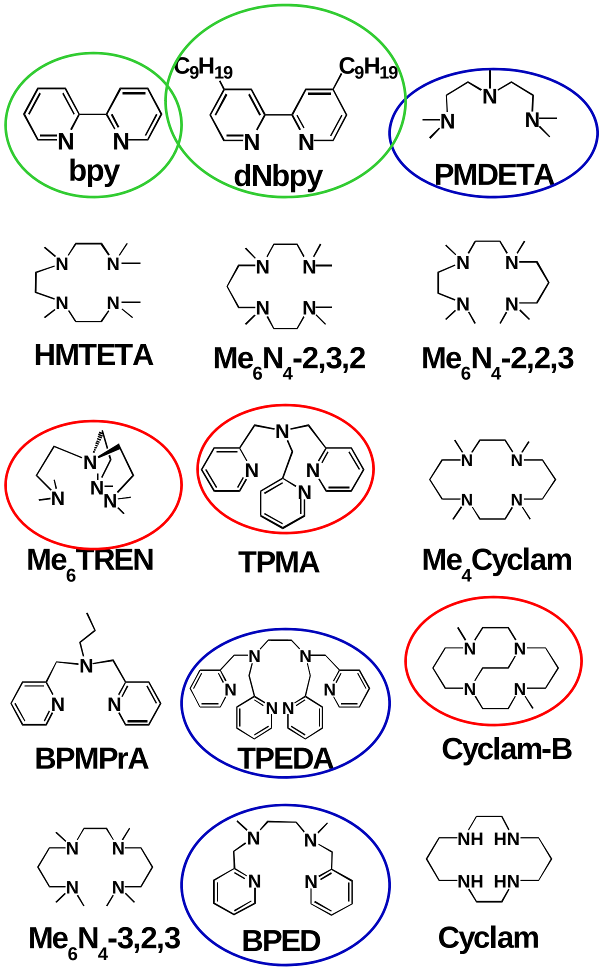


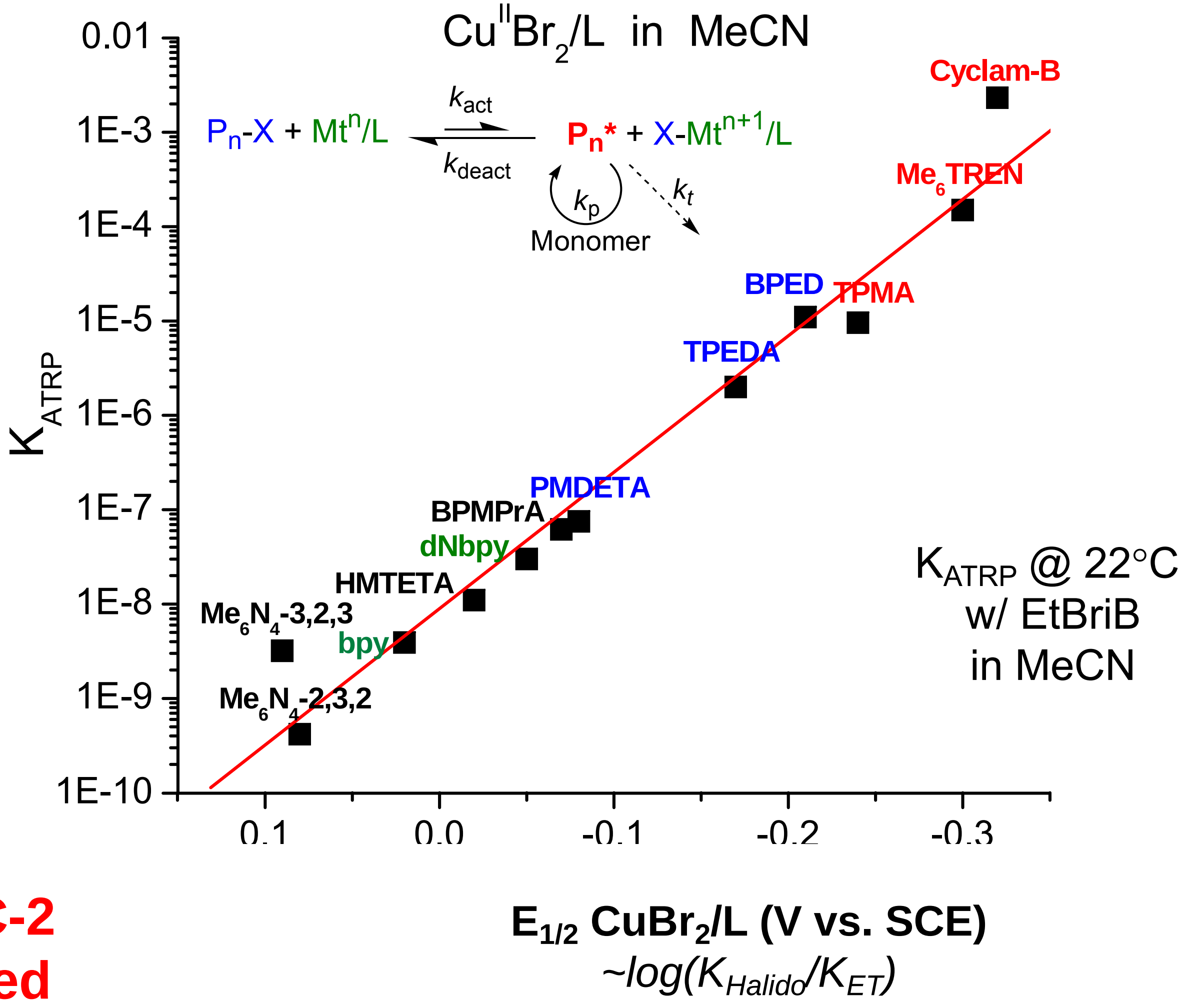
St / Ini / CuCl / dNbpy
500 / 1 / 0.01 / 0.02

# $K_{ATRP}$ and Electrochemistry

$K_{ATRP} = (\cancel{K_{BH}}\cancel{K_{EA}}K_{Halido})/K_{ET}$

0.059 V ~ 1 order of magnitude $K_{ET}$



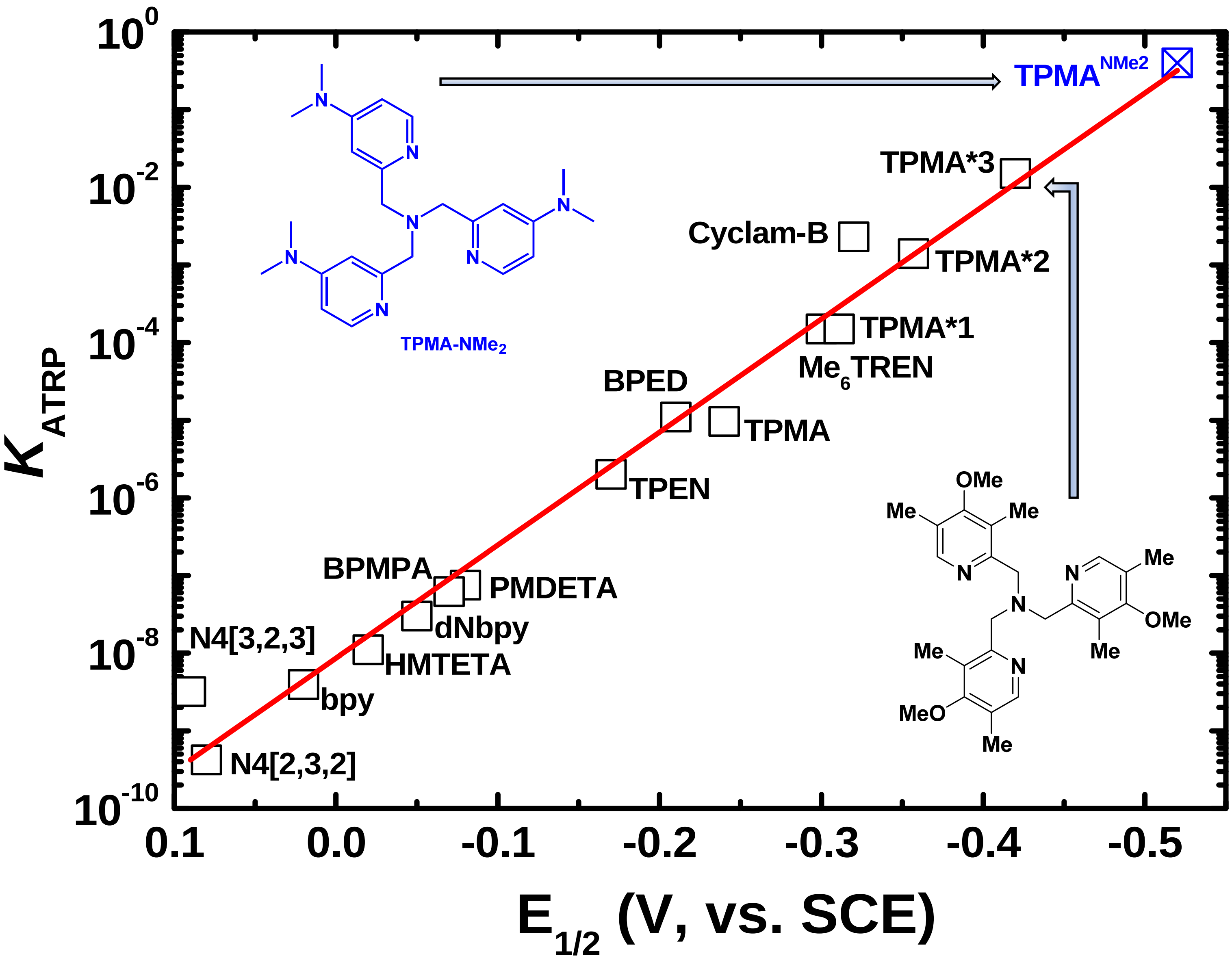


**$N_2<N_3<N_4$, C-4<C-3<C-2**

**linear<cyclic<branched**

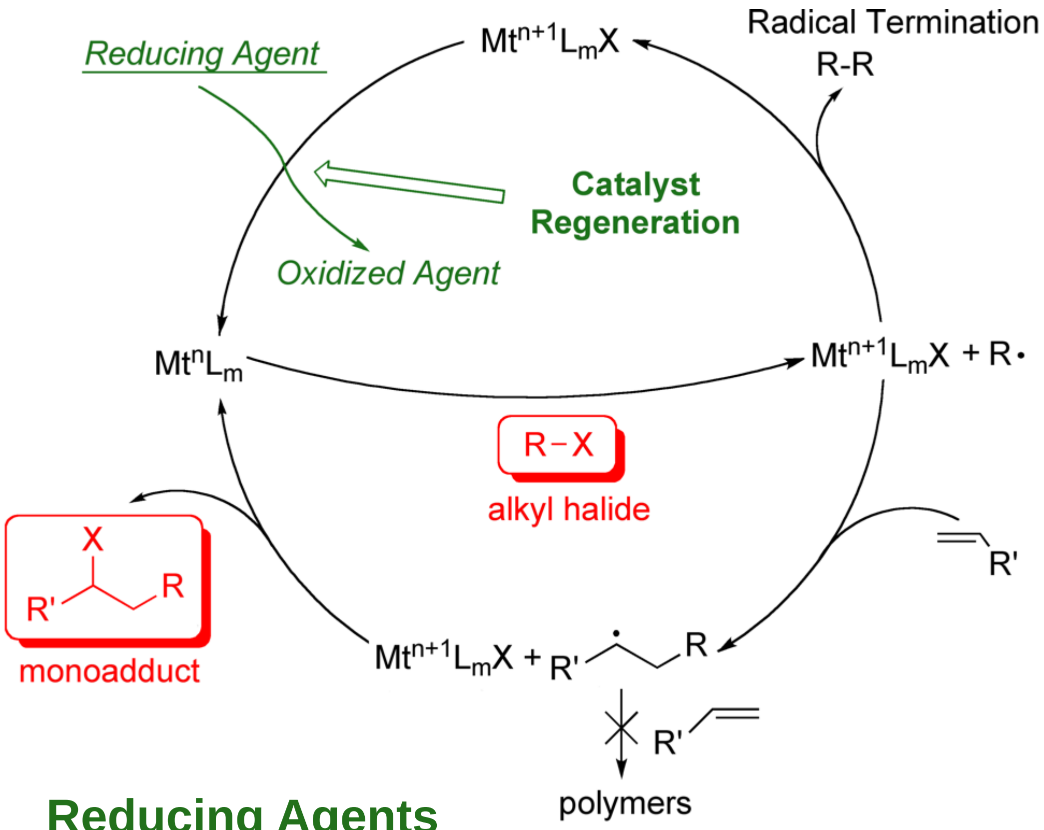
**ar. amine<imine<pyr~alk. amine**

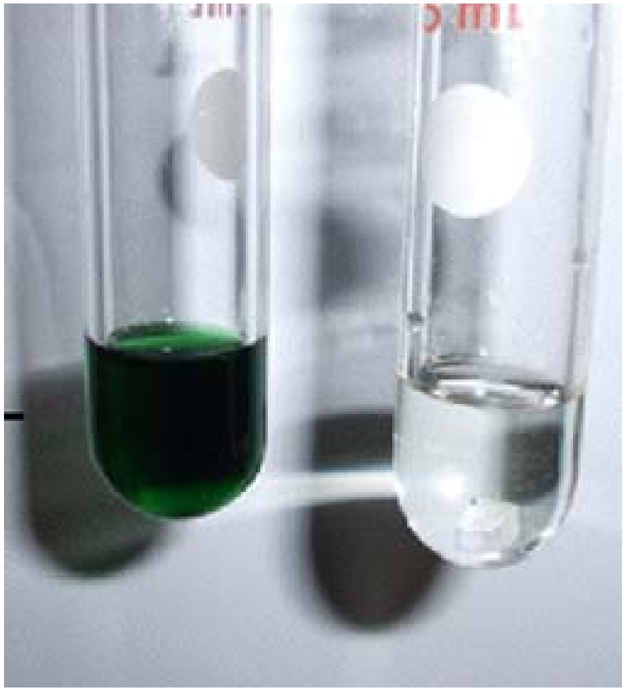
$k_a$ for MBrP in MeCN = 4 × $10^6$ $M^{-1}$ $s^{-1}$.
$K_{ATRP}$ ~ 0.4, => $k_{da}$ ~ 1 × $10^7$ $M^{-1}$ $s^{-1}$.



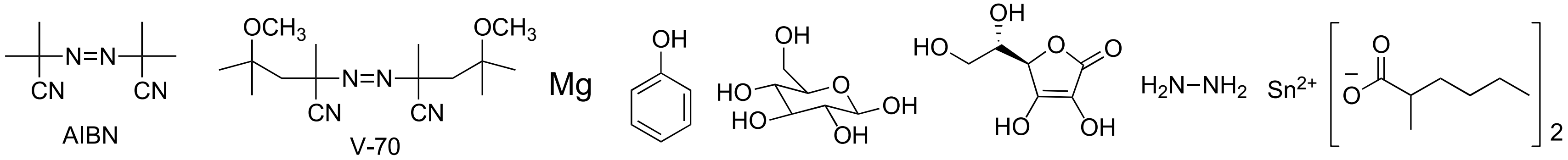
Dependence of $K_{ATRP}$ on the half-wave potential ($E_{1/2}$) of the $Cu^{II}Br_2/L$ complexes. Measured with ethyl α-bromoisobutyrate in MeCN.
Data from JACS *130* (2008) 10702 & JACS *140* (2018) 1525.

# Catalyst Regeneration in ATRA with Reducing Agents
# From ICAR/ARGET ATRP to ATRA (*aller-retour*)





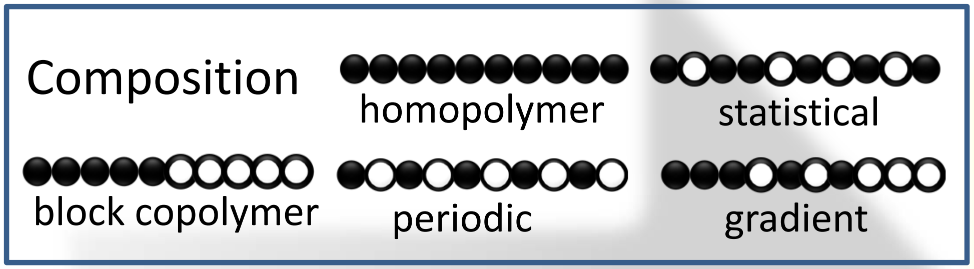
**Reducing Agents**



**& eATRA!!**

Pintauer, T.; Matyjaszewski, K., *Chem. Soc. Rev.* ***2008,*** *37, 1087-1097.*

# Soft Polymeric Materials with Complex Architecture & Controlled Heterogeneity



Composition

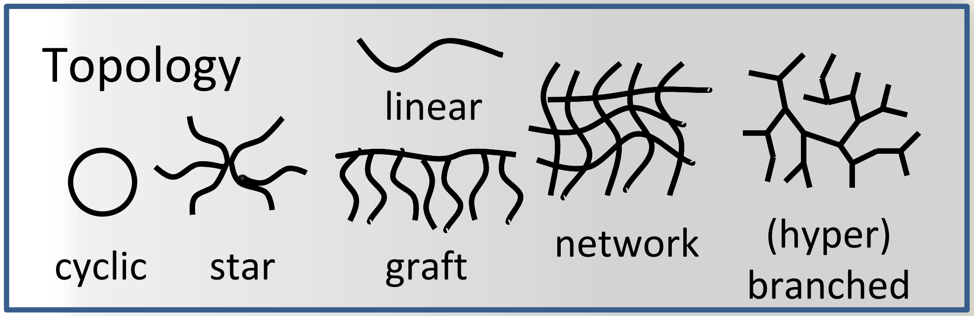
homopolymer

statistical

block copolymer

periodic

gradient



Topology

linear

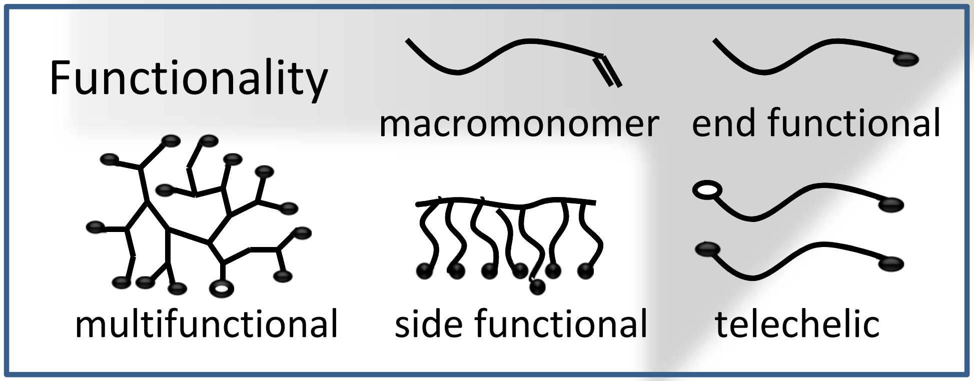
cyclic

star

graft

network

(hyper) branched



Functionality

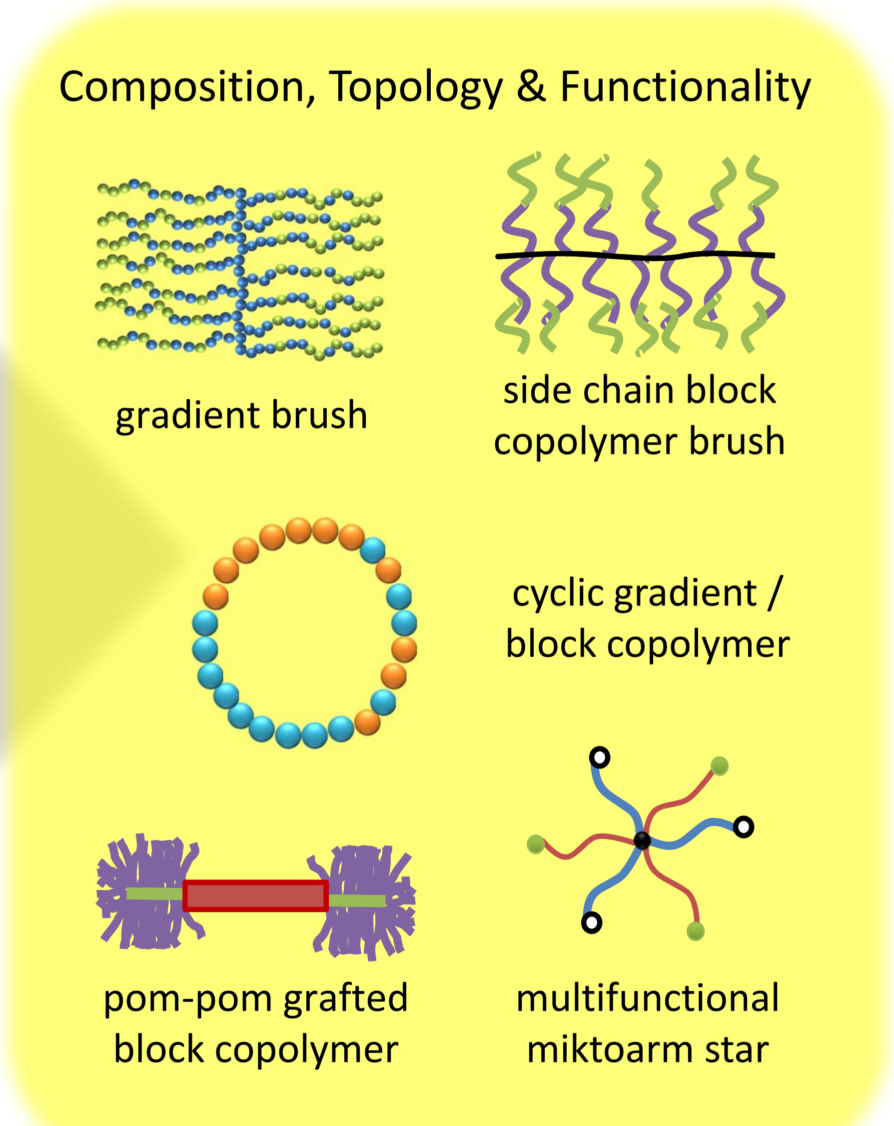
macromonomer

end functional

multifunctional

side functional

telechelic



Composition, Topology & Functionality

gradient brush

side chain block copolymer brush

cyclic gradient / block copolymer

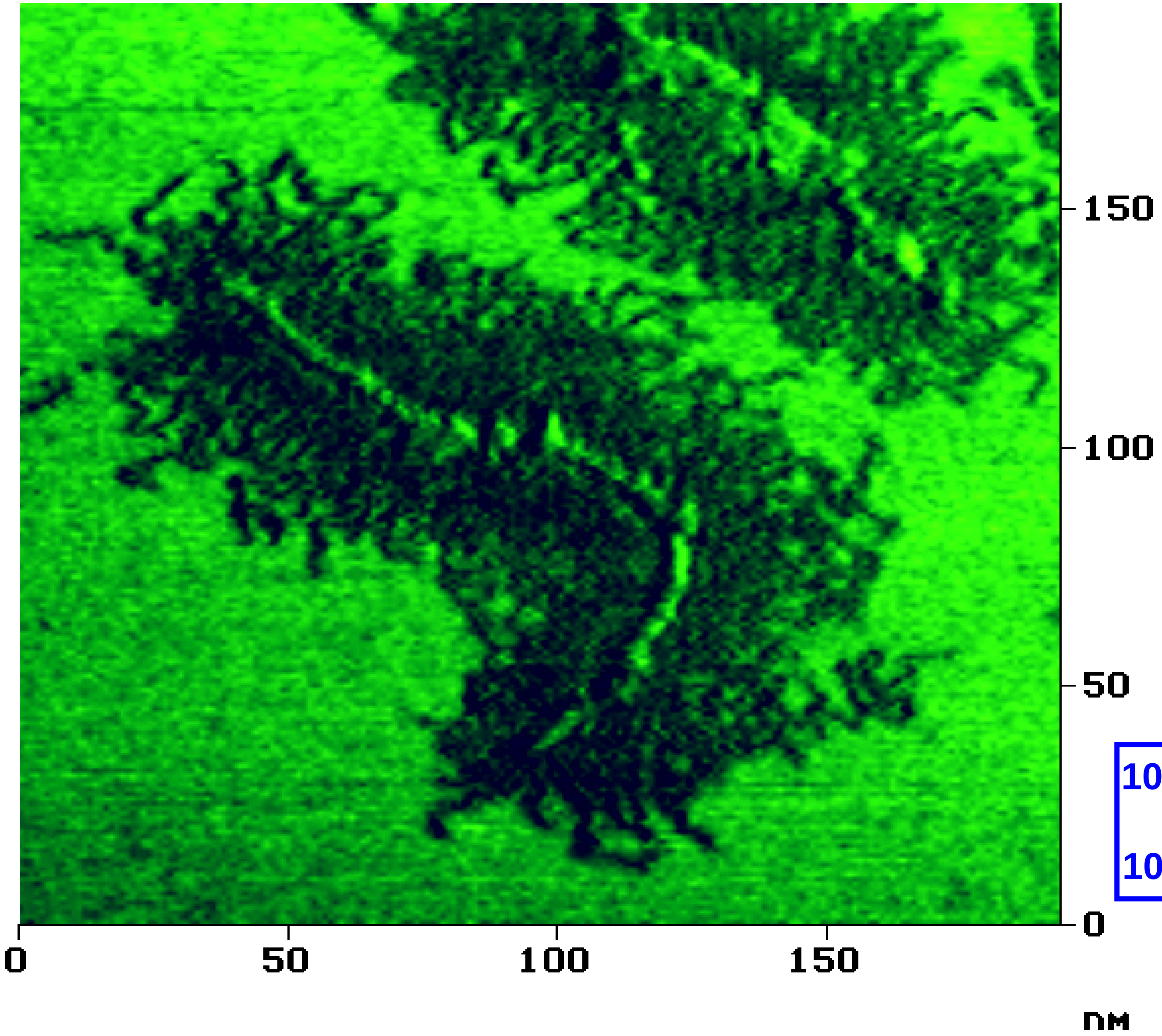
pom-pom grafted block copolymer

multifunctional miktoarm star

Science, 2011, 333, 1104

**& VARIOUS HYBRIDS**

# Example of Nanostructured Material: pBA Brush



**AFM of a Single Molecule!**

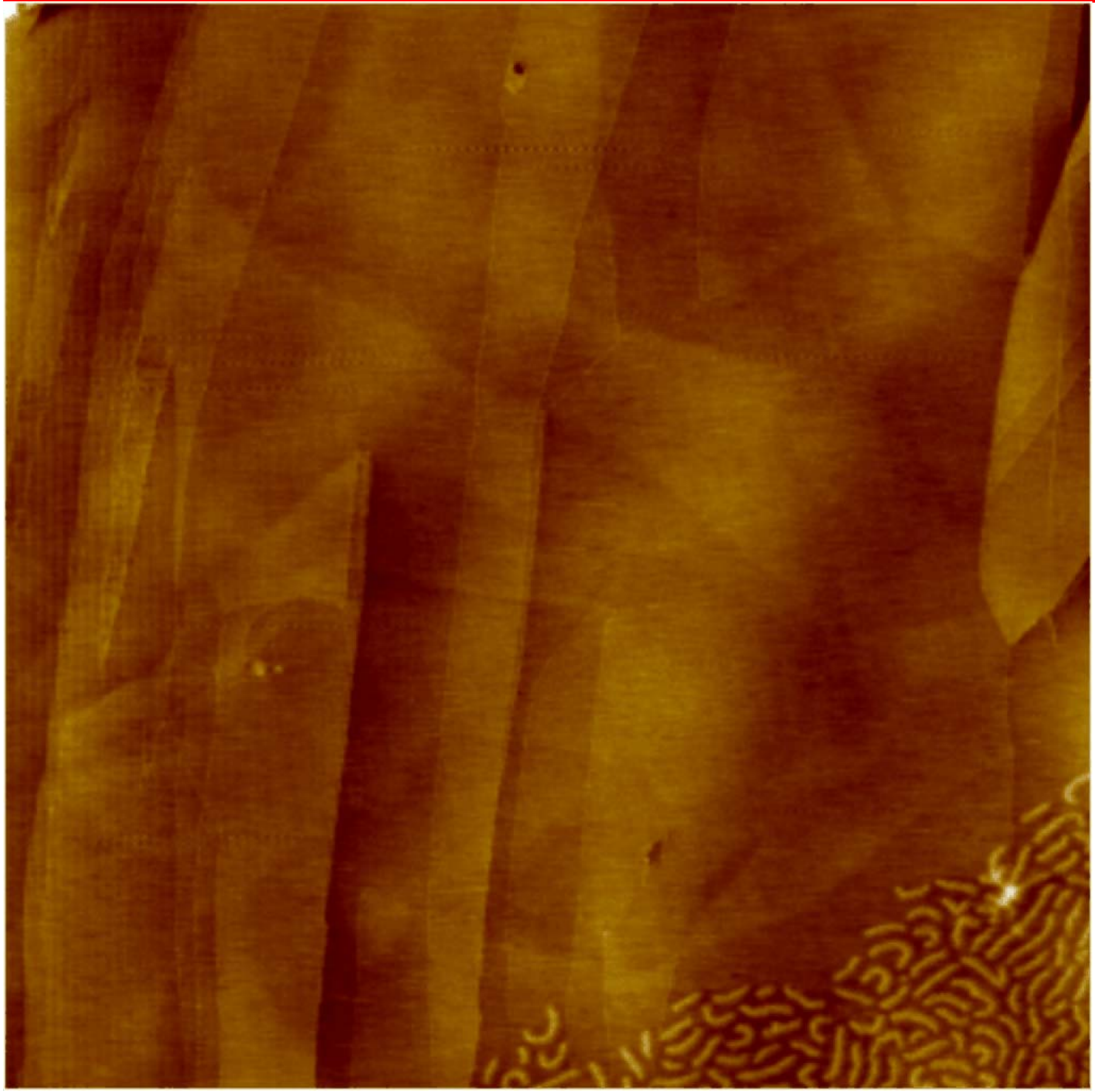
**Backbone:**
**methacrylate**
**DP=400**
**PDI=1.2**

**Side Chains:**
**poly(butyl acrylate)**
**DP=40**
**overall PDI=1.2**
**overall $M_n$~2,000,000**

**100 nm => 10 cm**
**~**
**10 cm => 100 km**

S. Sheiko, UNC

# Spreading of Soft pBA Brush Monolayer ($T_g$= -50 °C)



pBA brushes (N=567, n=51)

Substrate: graphite

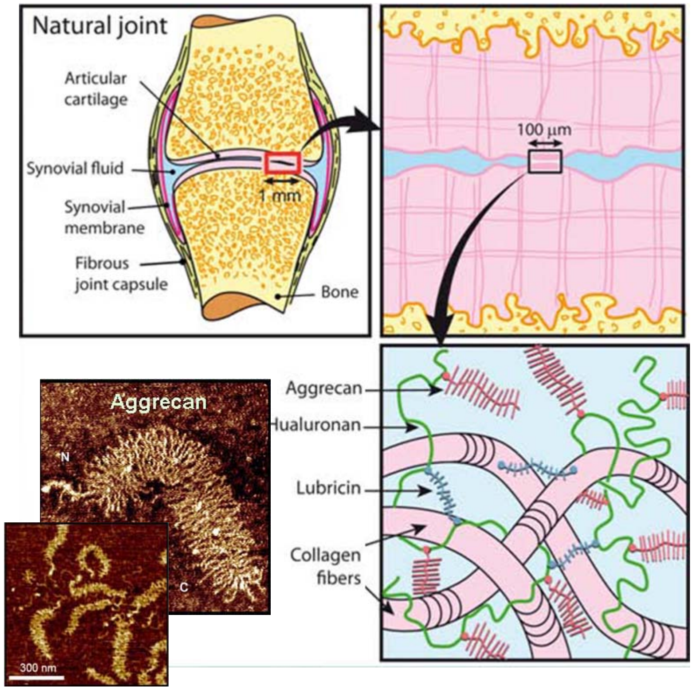
Temperature: RT

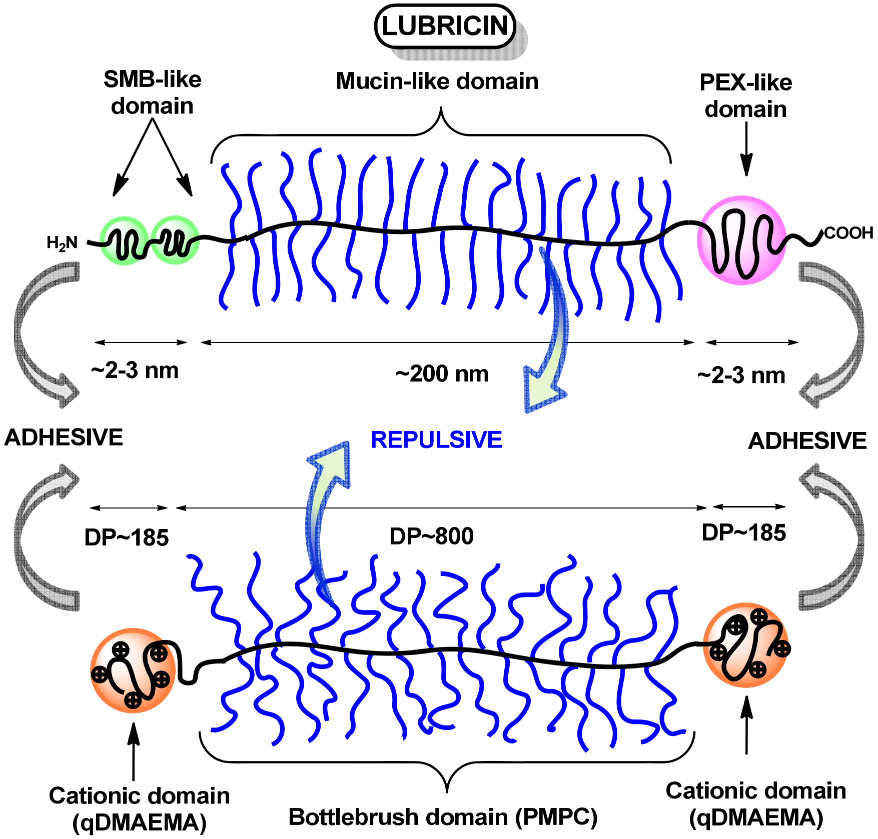
Frame: 3μ x 3μ

Duration: 10 hours

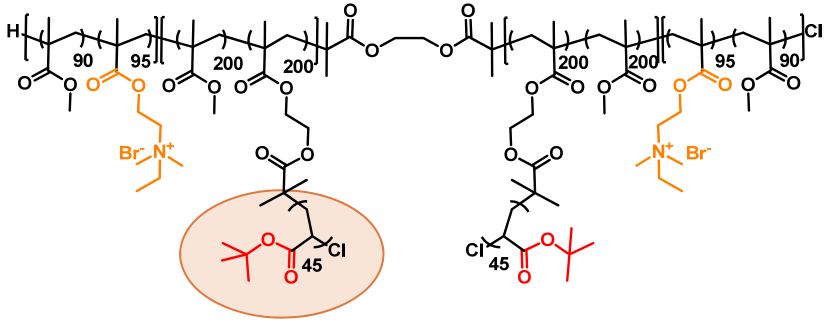
S. Sheiko, M. Rubinstein

# Lubrication in Joints

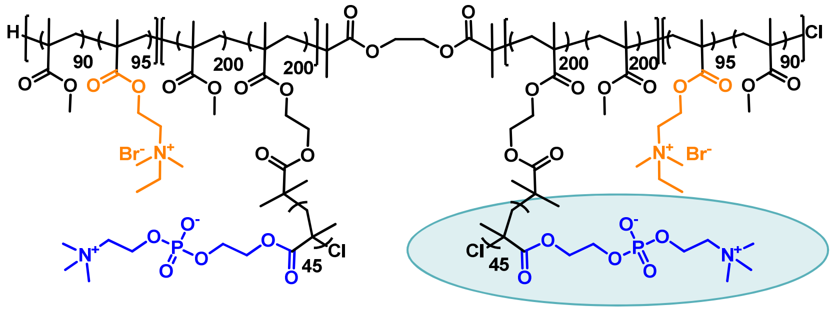




**ABA Bottlebrush - Hydrophobic**



**ABA Bottlebrush - Hydrophilic**

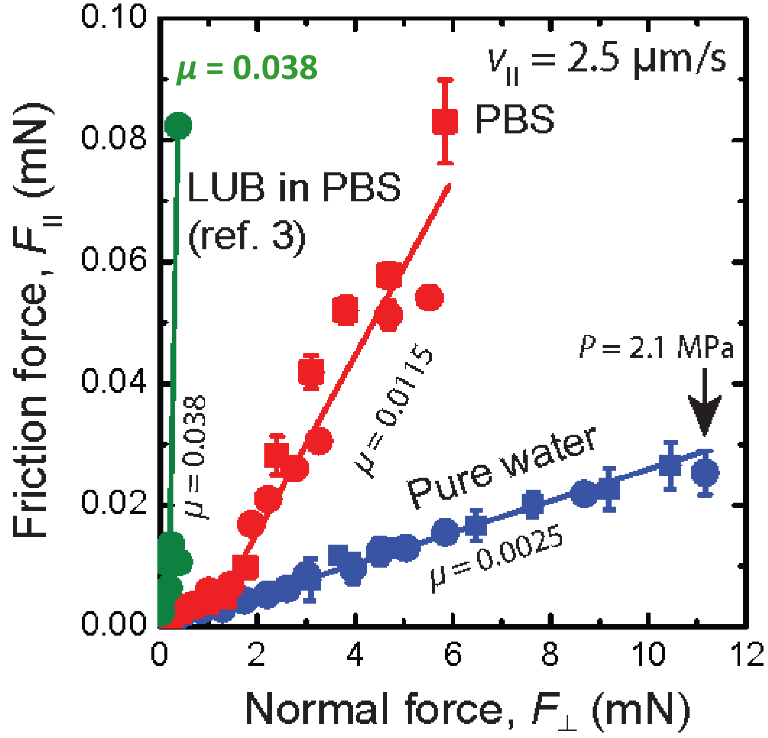


**w J. Israelachvili**

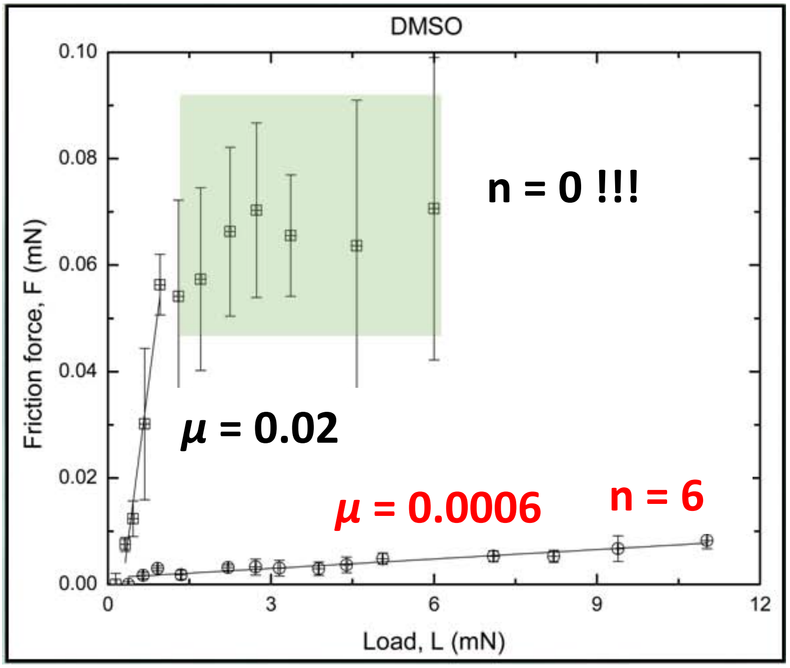
# Artificial Lubricin Properties

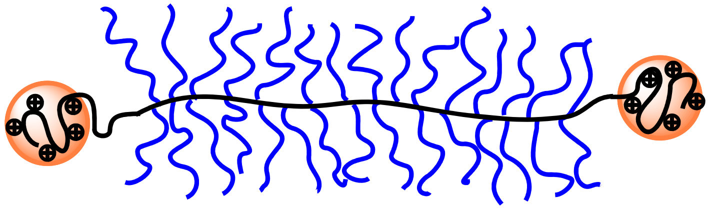
**C = 370 μg/ml**
**Mica surfaces**

**Hydrophilic, PMPC Grafts**



**Hydrophobic, PtBA Grafts**



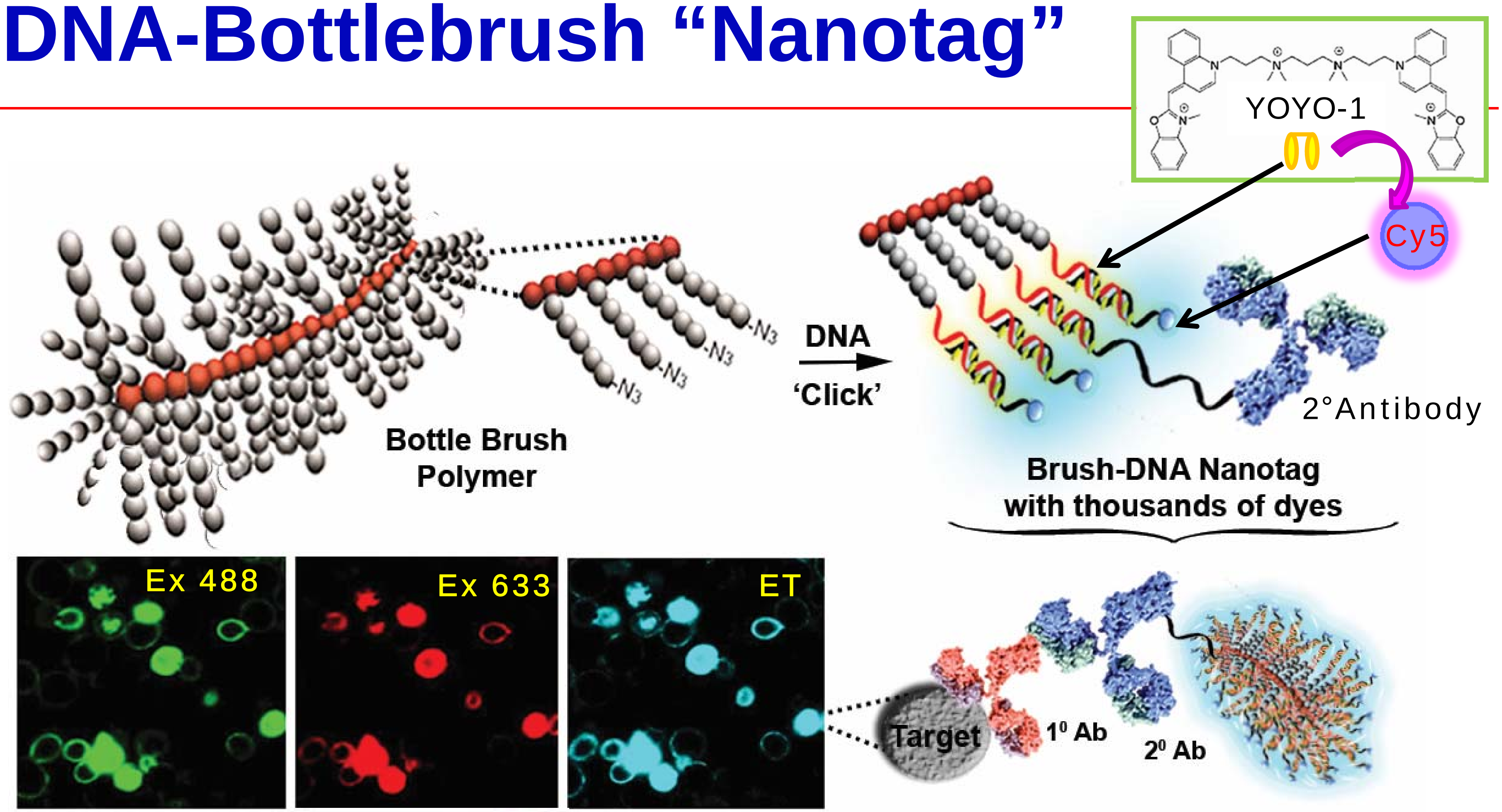


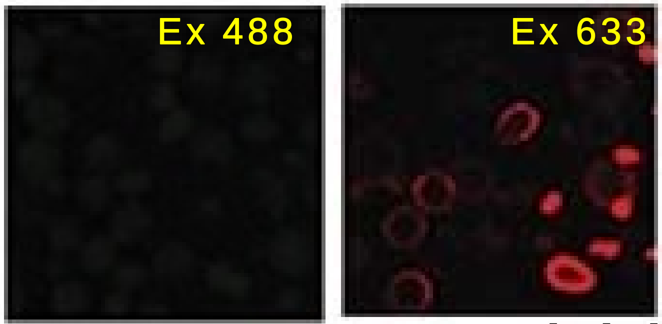
*J. Am. Chem. Soc.* ***2014, 136,*** *6199-6202.*

**Artificial Lubricin:**

- Low friction coefficient **$\mu$ = 0.0025** in water and **$\mu$ = 0.0006!** in DMSO at **20 atm**
- Pressure in knee joints **~2 atm** (100 kg, 2x5cmx5cm)
- ABA brush could sustain up to **~1 ton**
- Better performance than natural lubricin **$\mu$ = 0.038** at **0.4 atm**

# DNA-Bottlebrush "Nanotag"





Labeled with commercial QD655-Antibody

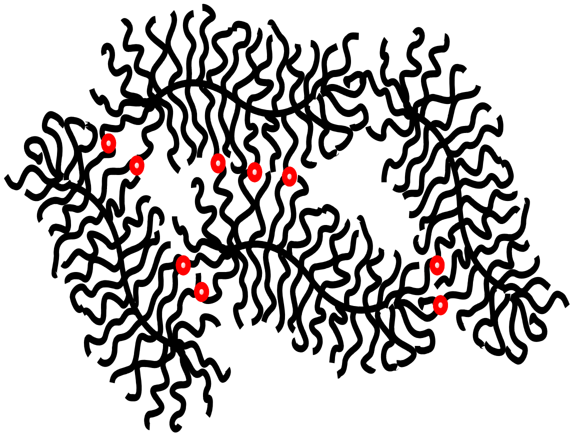
**with S. Das & B. Armitage**

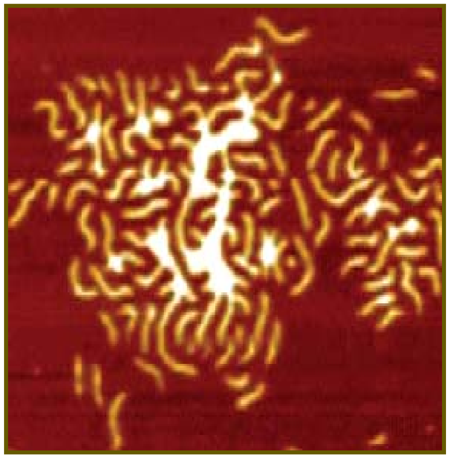
**Nanotags are ~ 100X brighter than any commercial antibody probe**

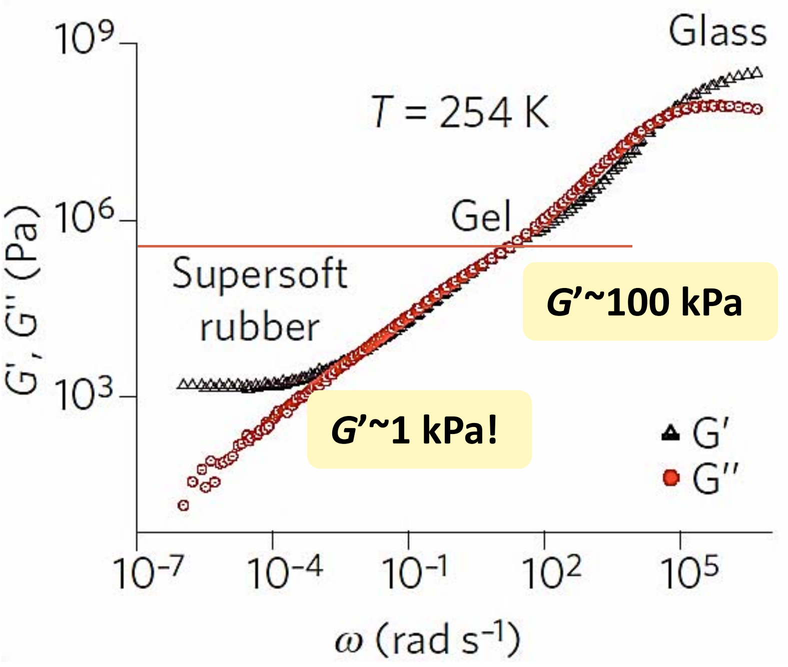
# Supersoft Elastomers from Bottlebrushes

with T. Pakula
S. Sheiko

**CROSS-LINKED BRUSHES**



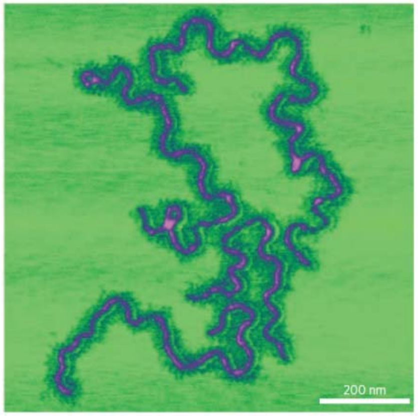


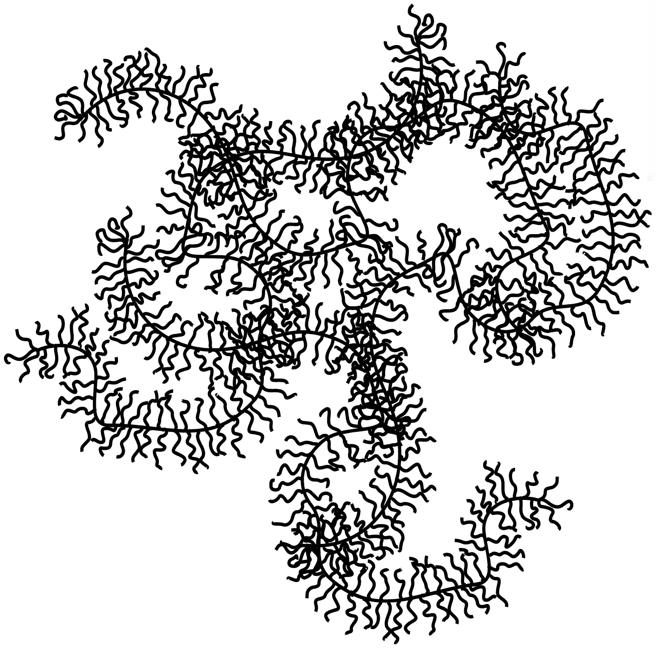


***G'*~100 kPa**

***G'*~1 kPa!**

**LONG BRUSHES**



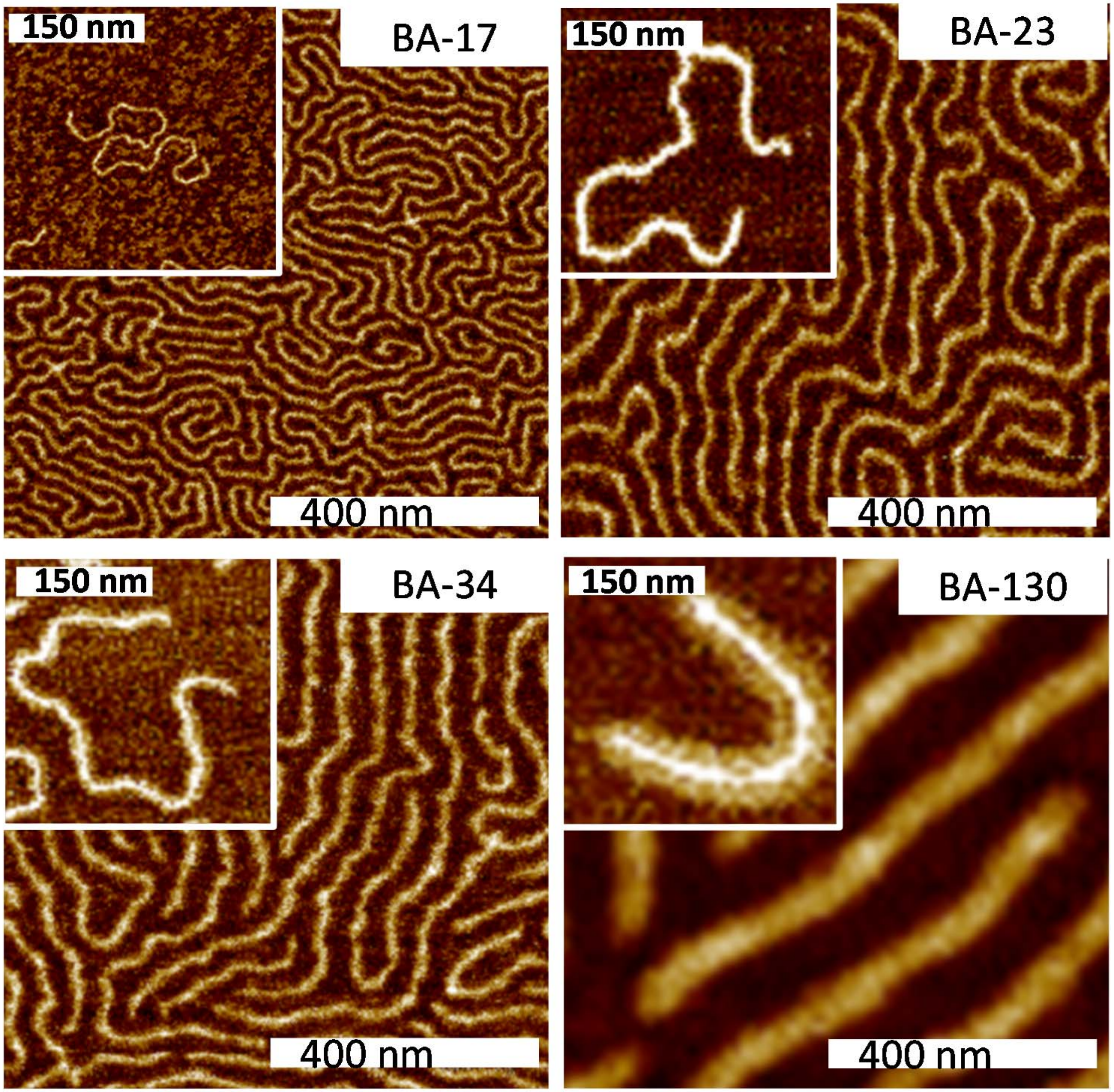


## Brush Super-soft Elastomers:

- ☐ **G' ~ 1kPa, as hydrogels**
- ☐ **Swollen by their own side chains – do not dry or leak**
- ☐ **Intraocular lenses, wound healing, tissue, conductive materials**

. *Macromolecules* **2007,** *ACS MacroLetters,* **2013**.

# AFM of Long Bottlebrushes



**Sergei Sheiko,**
**Univ. of North Carolina**

**AFM micrographs of**

**LB monolayers on**

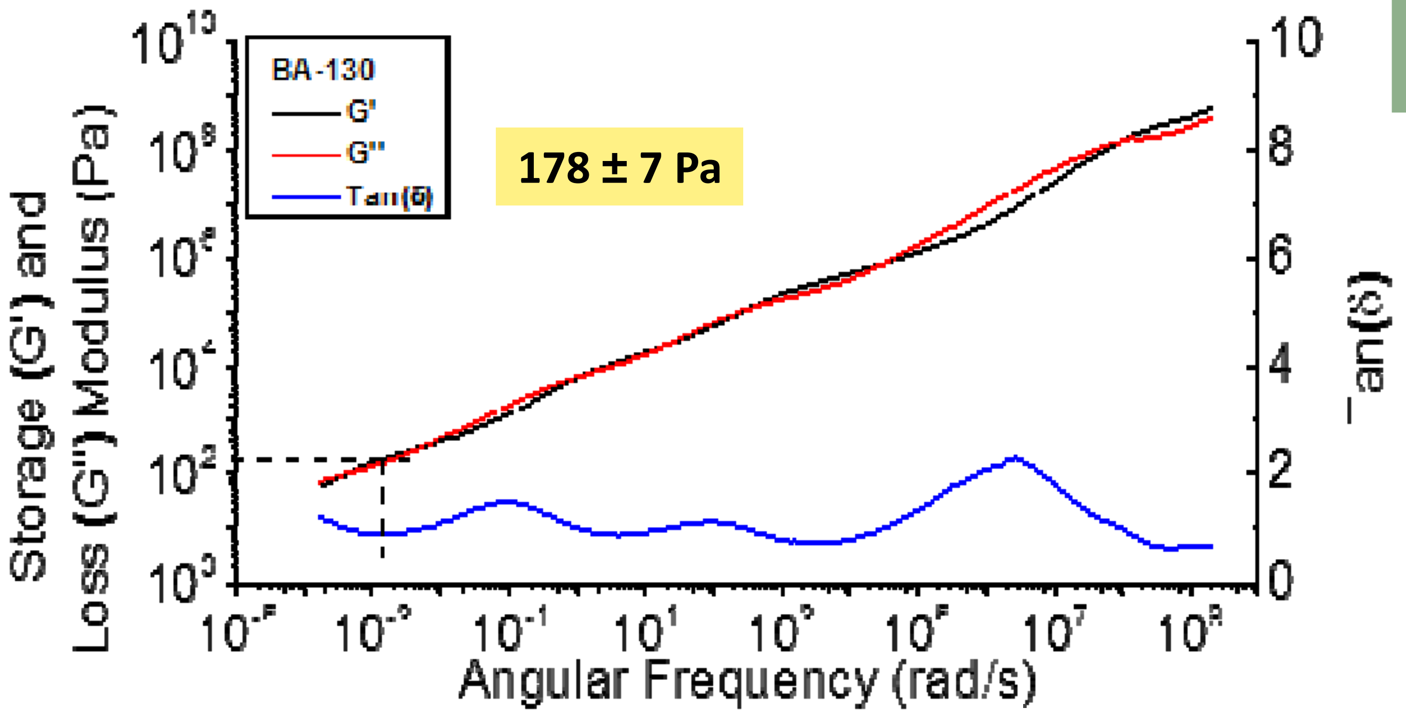
**mica surface**

**Long Bottlebrushes:**

☐ DP$_{bb}$=2200
☐ Variable DP$_{sc}$
☐ LB and spin cast
☐ High purity
☐ Increasing intermolecular distance
☐ Worm-like to rod-like topologies
☐ Increased persistence length

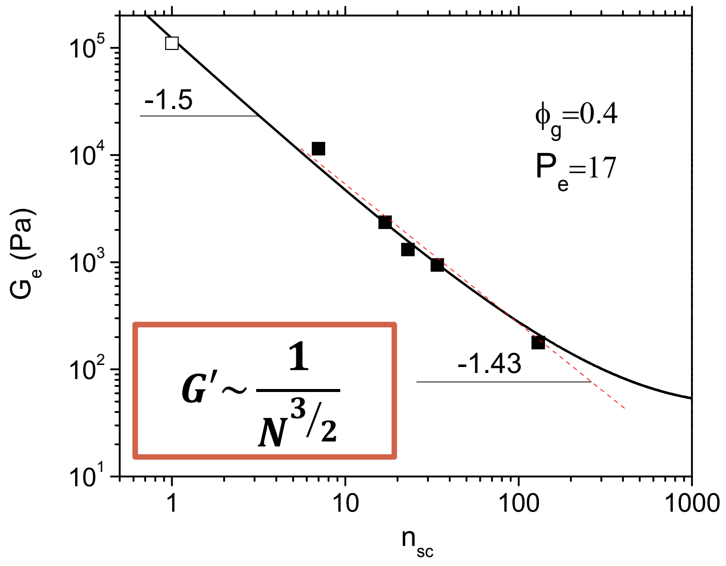
# DMA of Long & Thick Bottlebrushes

S. Sheiko,
M. Rubinstein
A. Dobrynin



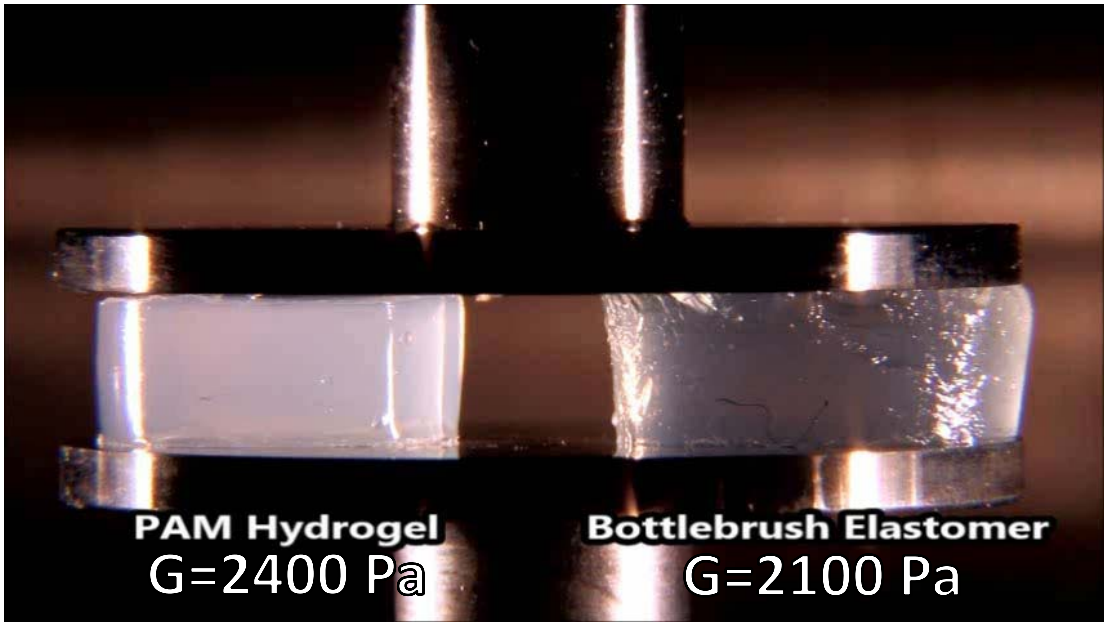
**178 ± 7 Pa**

| Sample | $G_e$, Pa | tan(δ) | $n_e$ | $n_{bb}/n_e$ | Plateau range $\log_{10}$ (rad/s) |
|---|---|---|---|---|---|
| **BA-4** | **11432 ± 331** | 0.49 ± 0.020 | 461 | 4.4 | NA |
| **BA-17** | **2421 ± 75** | 0.71 ± 0.006 | 871 | 2.3 | 2.6 |
| **BA-23** | **1310 ± 54** | 0.72 ± 0.004 | 947 | 2.2 | 2.4 |
| **BA-34** | **938 ± 28** | 0.79 ± 0.005 | 1071 | 1.9 | 1.8 |
| **BA-130** | **178 ± 7** | 0.86 ± 0.013 | 1768 | 1.2 | 1.1 |



$$G' \sim \frac{1}{N^{3/2}}$$

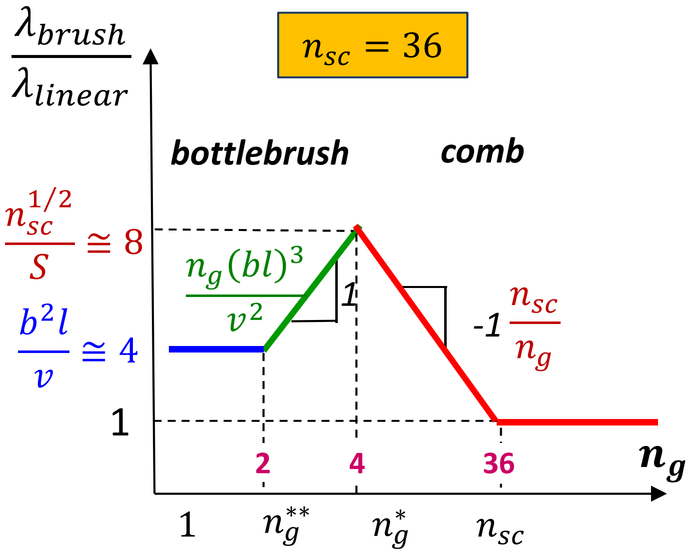
# Super-soft and Super-elastic



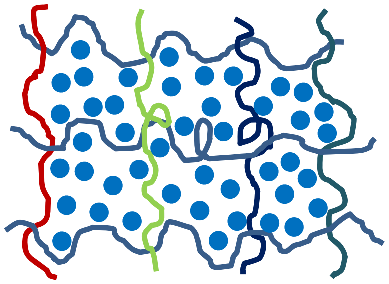
10% polymer

8% backbone

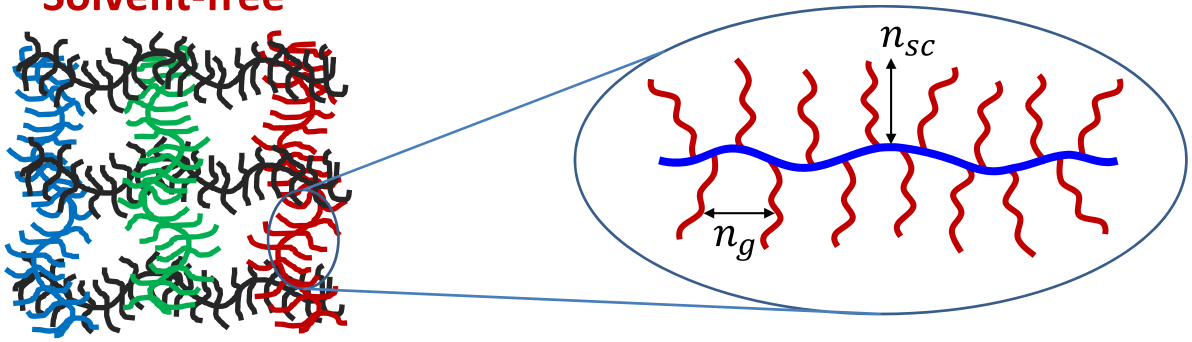
**Extension limit:** $\lambda = R_{max}/R_0$



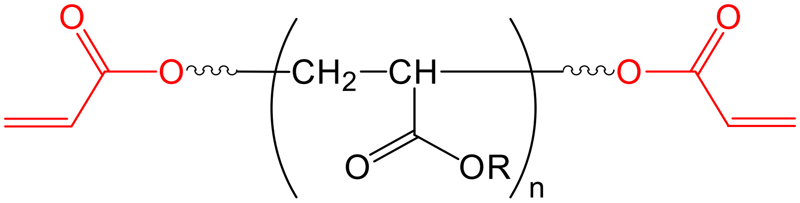
**Solvent-swollen**



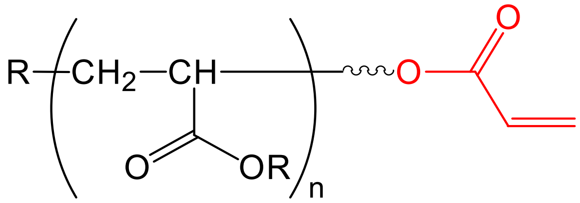
**Solvent-free**



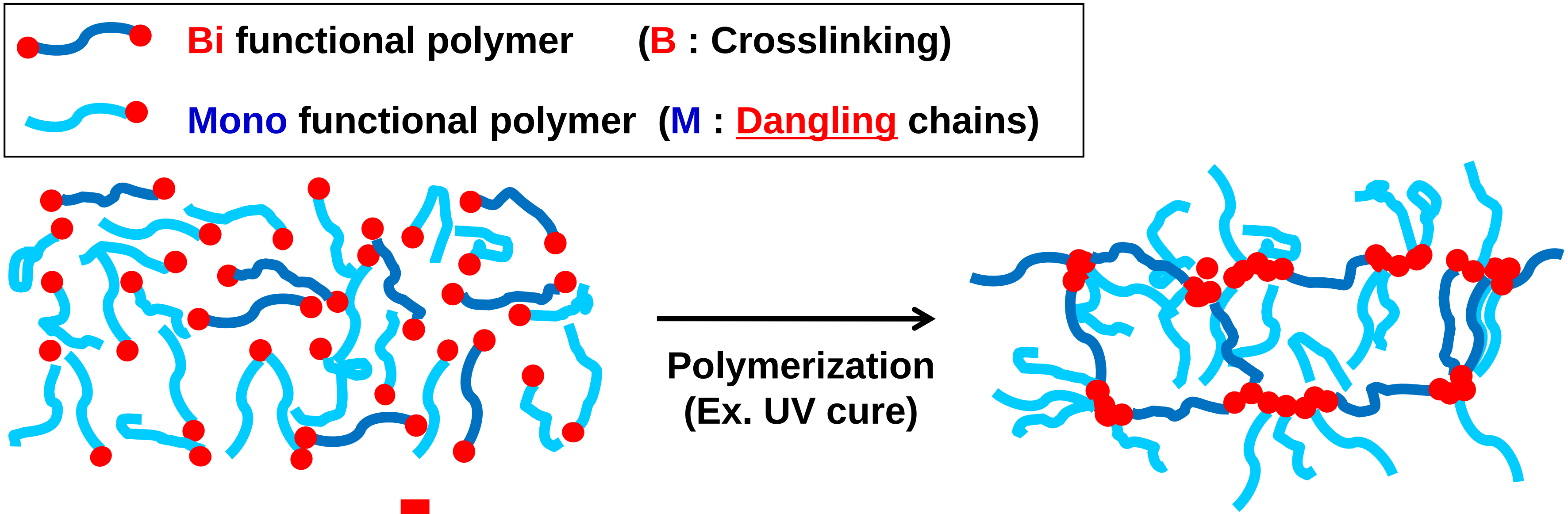
# Supersoft Gel



Difunctional polymer



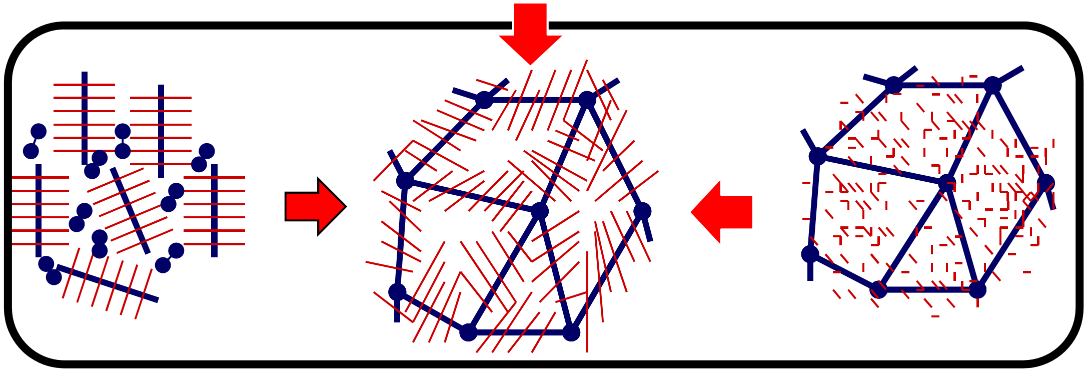
Monofunctional polymer



**Bi functional polymer (B : Crosslinking)**

**Mono functional polymer (M : Dangling chains)**

**Polymerization**
**(Ex. UV cure)**



**very loose polymer network**
**with well-controlled molecular**
**weight of dangling side chain**

Super Soft Gel Kaneka

# Supersoft Gel

| Properties | | SA-1 | SA-2 | Silicone gel |
|---|---|---|---|---|
| Hardness | DuroA | 22 | 0 | 0 |
| | DuroE | 35 | 2 | 0 |
| Compression set(150℃*70hrs) | | 9 | 31 | 61 |
| impact resilience(%) | | 30 | 1.9 | 14.4 |

# Bigger Challenge!

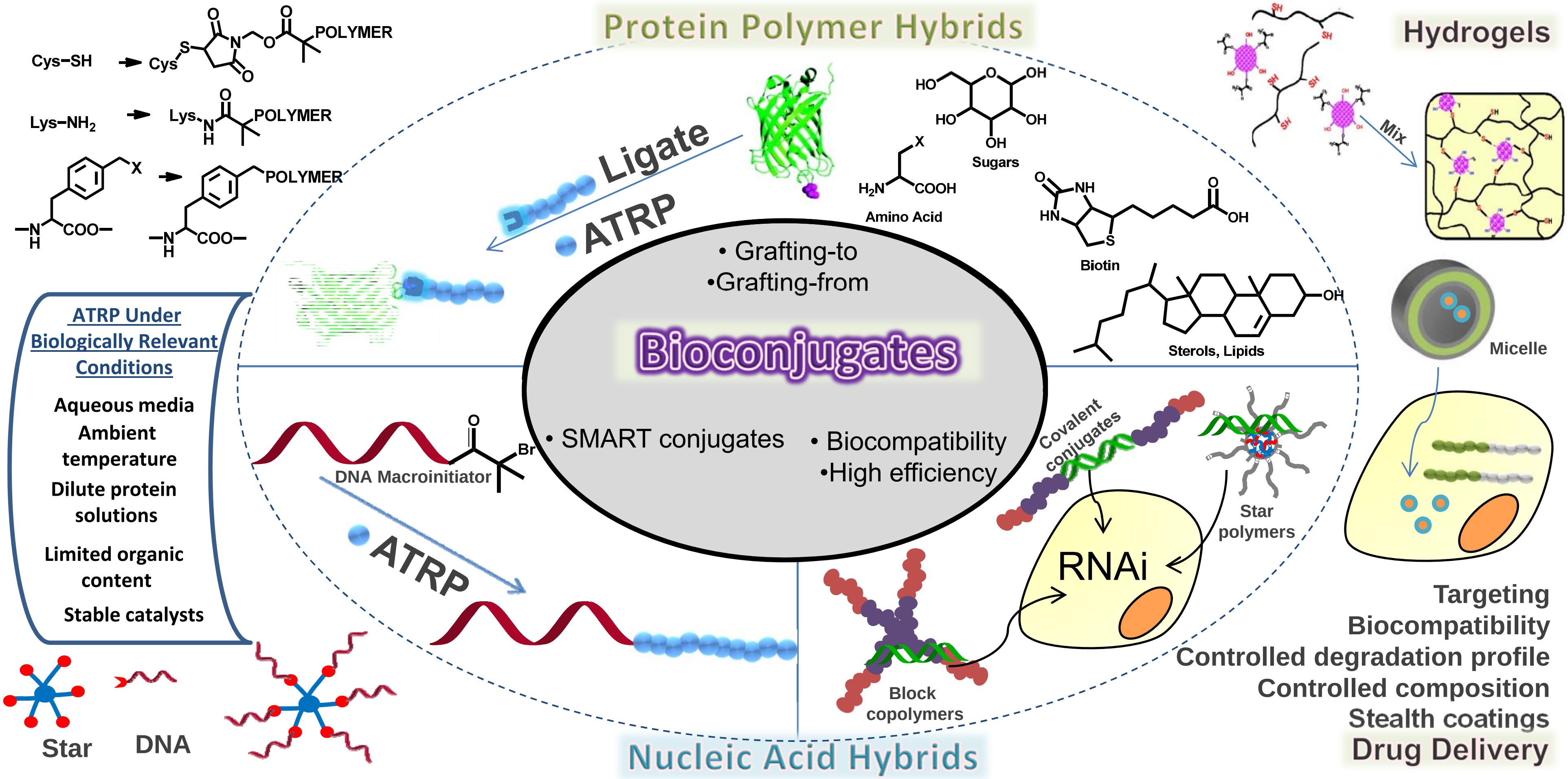
# PLATFORM CART

## FOR FRAGILE AND DELICATE ITEMS

# KANEKA SOFT MATERIAL

## EXAMINATION OF VIBRATION ISOLATOR

# Bio-Hybrids by ATRP



**Bioconjugates**

- Grafting-to
- Grafting-from
- SMART conjugates
- Biocompatibility
- High efficiency

**ATRP Under Biologically Relevant Conditions**

Aqueous media

Ambient temperature

Dilute protein solutions

Limited organic content

Stable catalysts

Targeting

Biocompatibility

Controlled degradation profile

Controlled composition

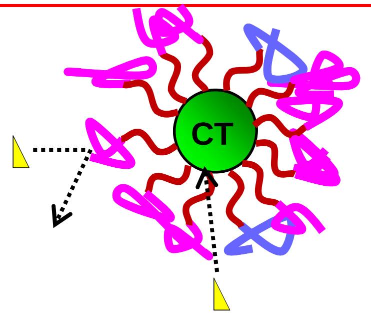
Stealth coatings

**Drug Delivery**

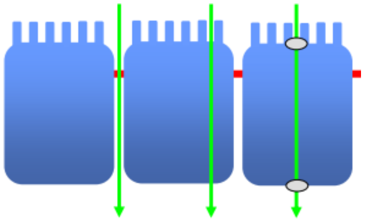
ATRP in the design of functional materials for biomedical applications, *Prog. Polym. Sci.* ***2012,*** *37, 18-37;*
Development of microgels/nanogels for drug delivery applications, *Prog. Polym. Sci.* ***2008,*** *33, 448-477;*
Biodegradable Nanogels Prepared by ATRP *J. Am. Chem. Soc.* ***2007,*** *129, 5939-5945;*
Star Polymers with a Cationic Core Prepared by ATRP for Cellular Nucleic Acids Delivery, *Biomacromolecules* ***2013,*** *14, 1262-1267;*
Preparation of Cationic Nanogels for Nucleic Acid Delivery, *Biomacromolecules* ***2012, 13,*** *3445-3449;*
A Protein-Polymer Hybrid Mediated By DNA, *Langmuir* ***2012, 28,*** *1954-1958;*
ATRP under Biologically Relevant Conditions: Grafting from a Protein, *ACS Macro Letters* ***2012,*** *1, 6-10;*
Genetically Encoded Initiator for Polymer Growth from Proteins, *J. Am. Chem. Soc.* ***2010,*** *132, 13575-13577.*

*Carnegie Mellon University*

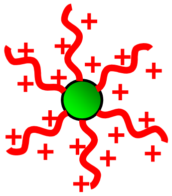
# High Density “Nano-armored” Enzyme Conjugates



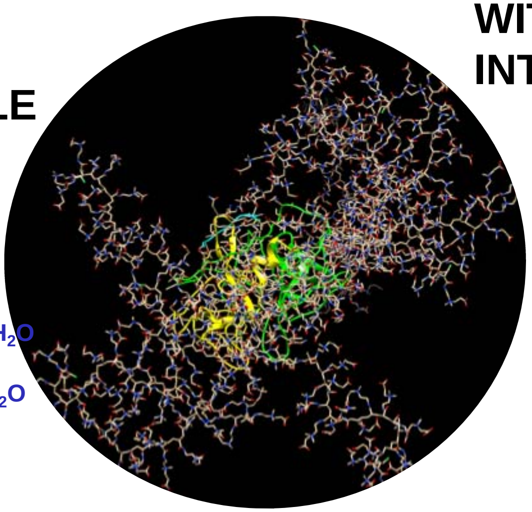
**RESPONSIVE**

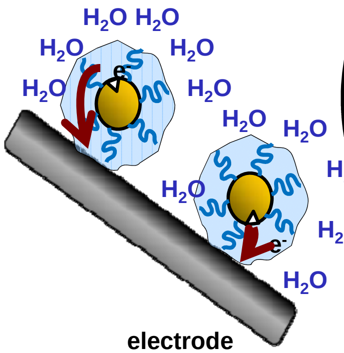


**STOMACH ACID STABLE WITH DOSE DEPENDENT INTESTINAL PERMEATION**



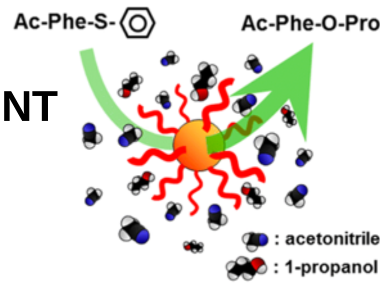
**THERMOSTABLE**





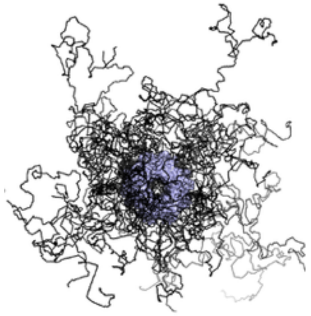
**CONDUCTIVE**

**ORGANIC SOLVENT SOLUBLE**

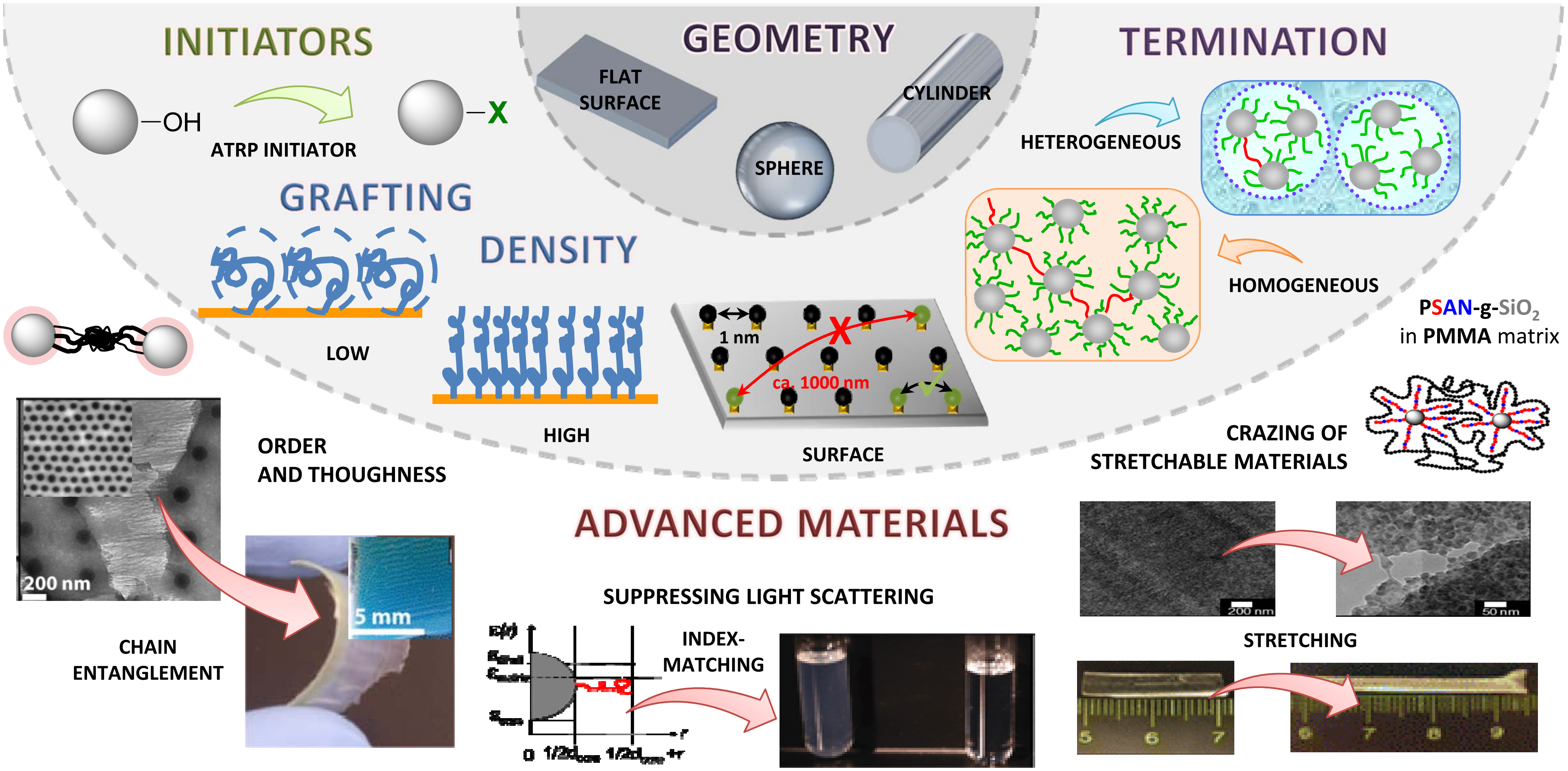


CT-pDMAEMA in Acetonitrile

**IMMUNO-ISOLATING**



# Organic/Inorganic Hybrids by ATRP



INITIATORS

—OH

ATRP INITIATOR

—X

GEOMETRY

FLAT SURFACE

SPHERE

CYLINDER

TERMINATION

HETEROGENEOUS

HOMOGENEOUS

GRAFTING DENSITY

LOW

HIGH

SURFACE

PSAN-g-$SiO_2$ in PMMA matrix

CRAZING OF STRETCHABLE MATERIALS

ORDER AND THOUGHNESS

CHAIN ENTANGLEMENT

ADVANCED MATERIALS

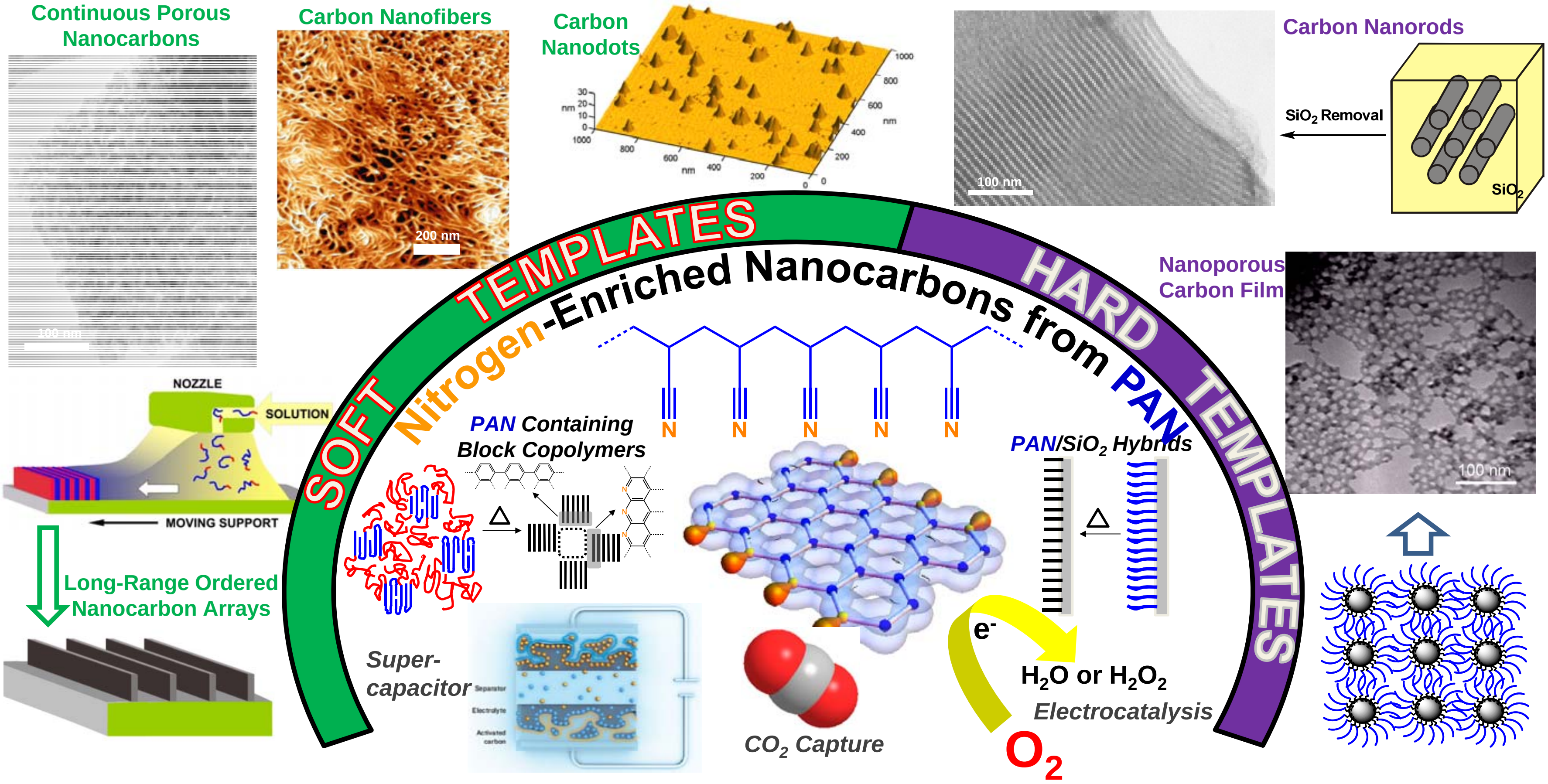
SUPPRESSING LIGHT SCATTERING

INDEX-MATCHING

STRETCHING

*Carnegie Mellon University*

# Nanostructured Carbons by ATRP



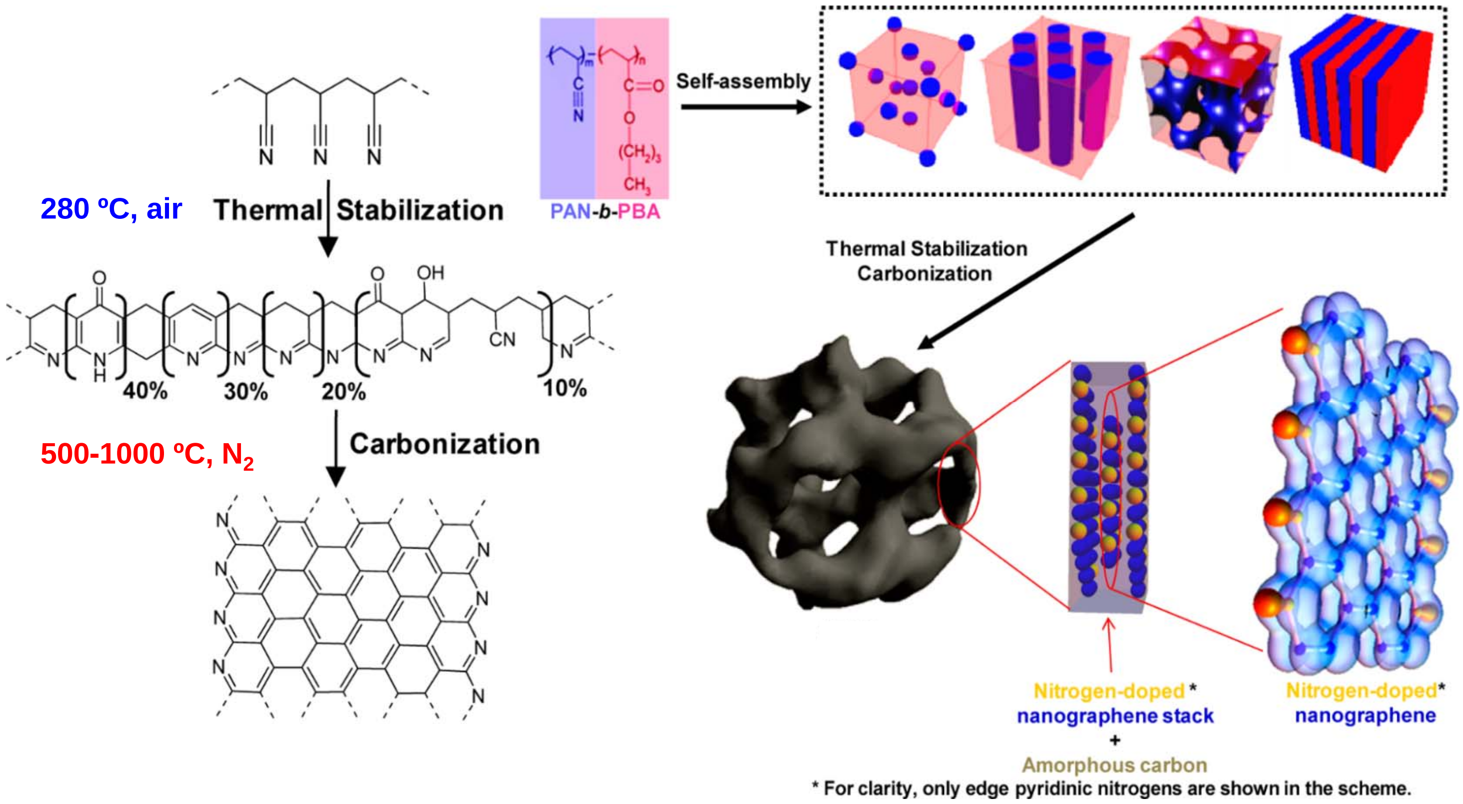
*J. Am. Chem. Soc*, **2002**, *124*, 10632;
*Angew. Chem. Int. Ed.* **2004**, *43*, 2783
*Chem. Mater.* **2006,** *18*, 1417
*Syn. Metal* **2009**, *159*, 177
*Macromol. Chem. Phys.* **2012**, *213*,1078
*ACS Macro Lett.* **2016**, *5*, 382

*Macromolecules* **2003**, *36*, 8587
*J. Phys.Chem.* **2005**, *109*, 9216
*Microp. & Mesop. Mater.* **2007**, *102*, 178
*J. Am. Chem. Soc* **2012**, *134*, 14846
*Mater. Horiz.* **2014**, *1*, 121

*Macromolecules* **2003**, *36*, 1465
*J. Am. Chem. Soc.* **2005**, *127*, 6918
*Adv. Mater.* **2008,** *20*, 1516
*Chem. Commun.* **2012**, *48,* 11516
*J. Mater. Chem. A* **2015**, *3*, 4413

*Angew. Chem.*, **2014**, *53*, 3957
*Chem. Sci.* **2014**, *5*, 3315
*J. Am. Chem. Soc.* **2015**, *137*, 13256
*J. Am. Chem. Soc.* **2014**, *136*, 480
*ACS Nano* **2012**, *6*, 6208

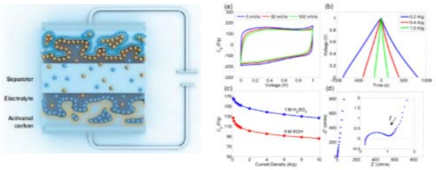
# N-Enriched Porous Nanocarbons from PAN-Containing Block Copolymers



* For clarity, only edge pyridinic nitrogens are shown in the scheme.

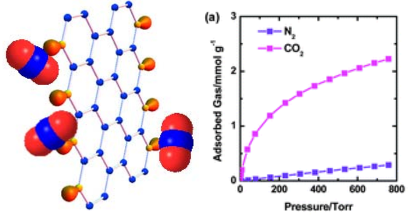
- Retention of morphology upon pyrolysis
- **Mesoporosity** from removal of sacrificial PBA block
- Surface area >1000 m$^2$/g
- Electrochemically active N atoms located on the edges of graphitic domains (d~10 nm)

**Supercapacitors**



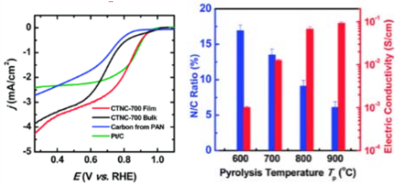
*J. Am. Chem. Soc.* **2012**, *134*, 14846

**$CO_2$ Sorbents**



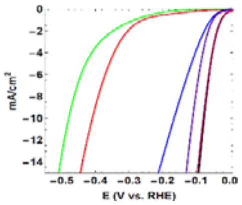
*Chem. Commun.* **2012**, *48*, 11516

**ORR**



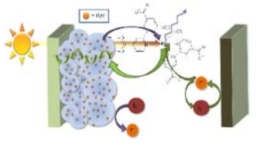
*Chem. Sci.* **2014**, *5*, 3315

**Hydrogen Evolution Reaction**



*ACS Appl. Mat. Interf.*, **2016**

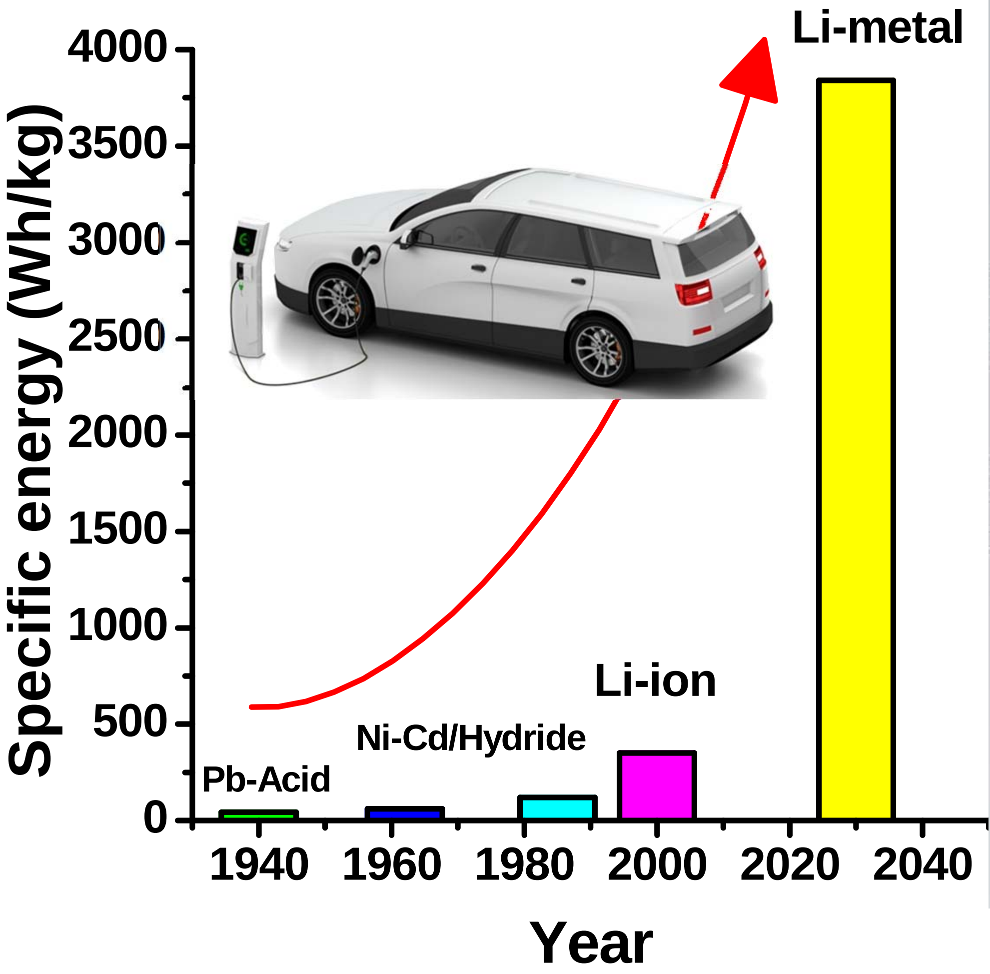
**Dye-Sensitized Solar Cells**



*J. Mater. Chem. A* **2015**, *3*, 4413

# Lithium Metal Batteries (LMB): Holy Grail of Battery Industry

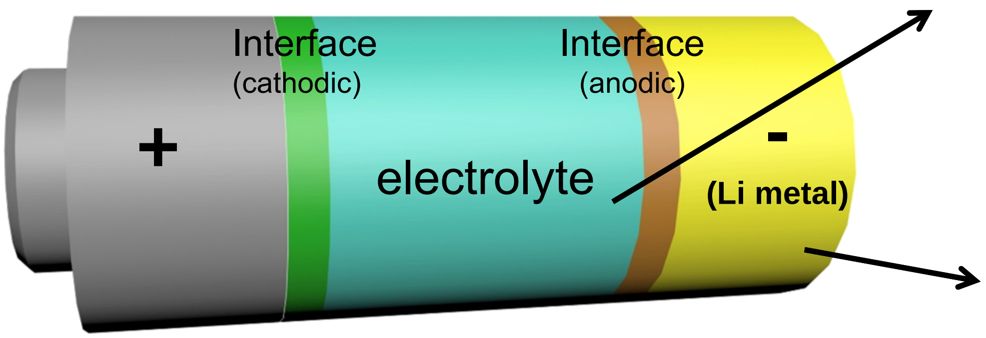
A lithium metal battery uses lithium metal as anodes instead of graphite



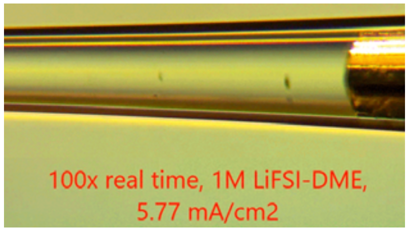
*SolidEnergy System*

# Polymers & Li Metal Batteries

A lithium metal battery uses **lithium metal** as anodes instead of **graphite**



Combustible electrolytes



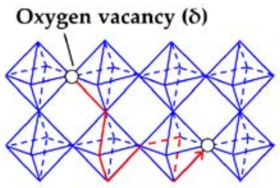
Dendrite growth

| **Role of polymer in** | **Li anode** | **Interface** (Designed SEI) | **Electrolytes** | **Cathode** |
|---|---|---|---|---|
| Research status | Barely explored | Very new | New wine old bottle | New challenges with new cathode |
| What polymers can do in each part? | 1. Lithium in polymer<br>2. Mitigate volume change (like Si)<br>3. Reduce Ohmic polarization<br>4. Improve contact | 1. Mitigate volume change<br>2. Reduce side-reaction between electrolytes and lithium | 1. Single-ion polymer<br>2. High conductivity in solid form<br>3. Polymers that tolerate high voltage | 1. Binder<br>2. Interface stability<br>3. Carbonized PAN with Sulfur<br>4. Polymers that tolerate high voltage |

# Inorganic/Polymer Composite Electrolytes

## Yttrium-Stabilized Zirconium Oxide (YSZ)

YSZ:
$(ZrO_2)_{0.92}.(Y_2O_3)_{0.08}$



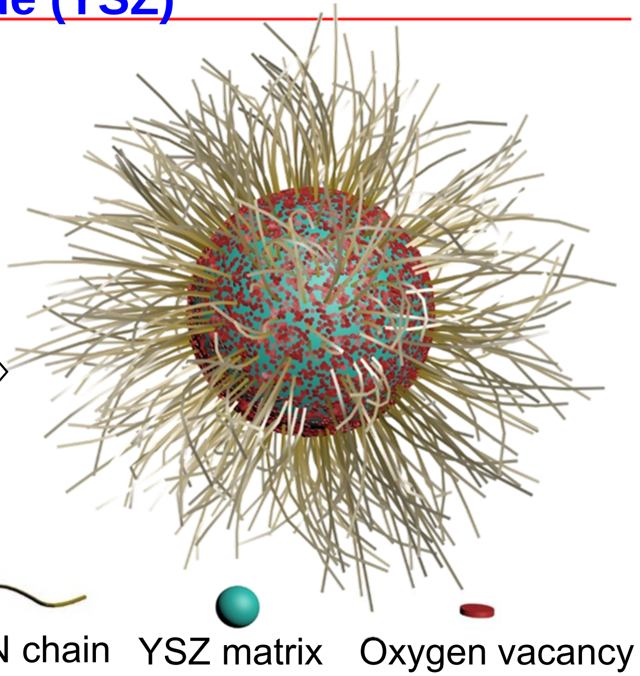
Oxygen vacancy:
1. Trap anions
2. Facilitate $Li^+$ transport

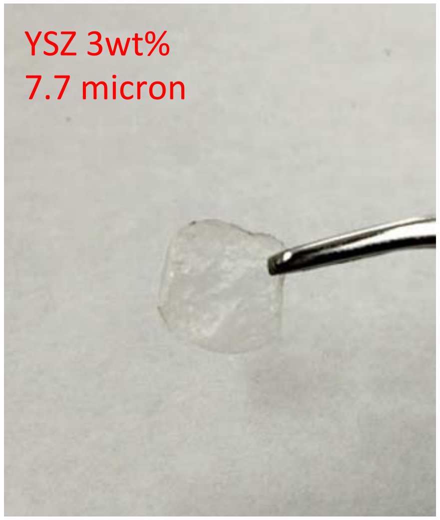
A **blend** of YSZ with PAN/$LiClO_4$

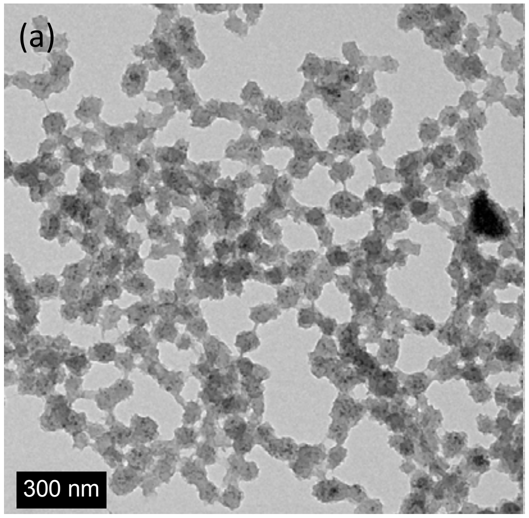
*Cui. Y., et al, ACS Nano, 2016, 10, 11407*

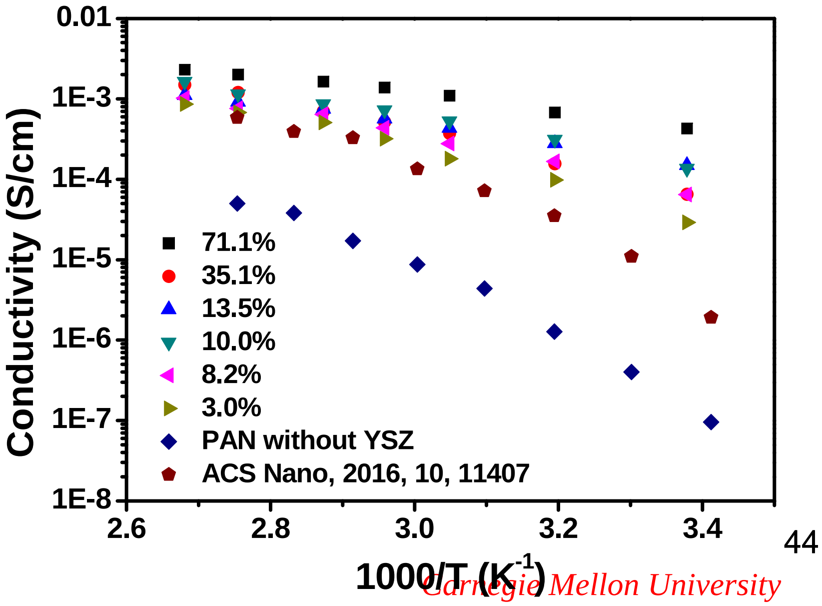
YSZ: 21 wt%

Grafted system



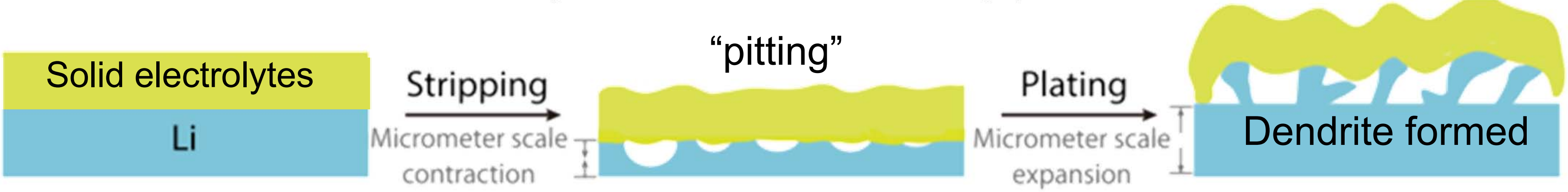






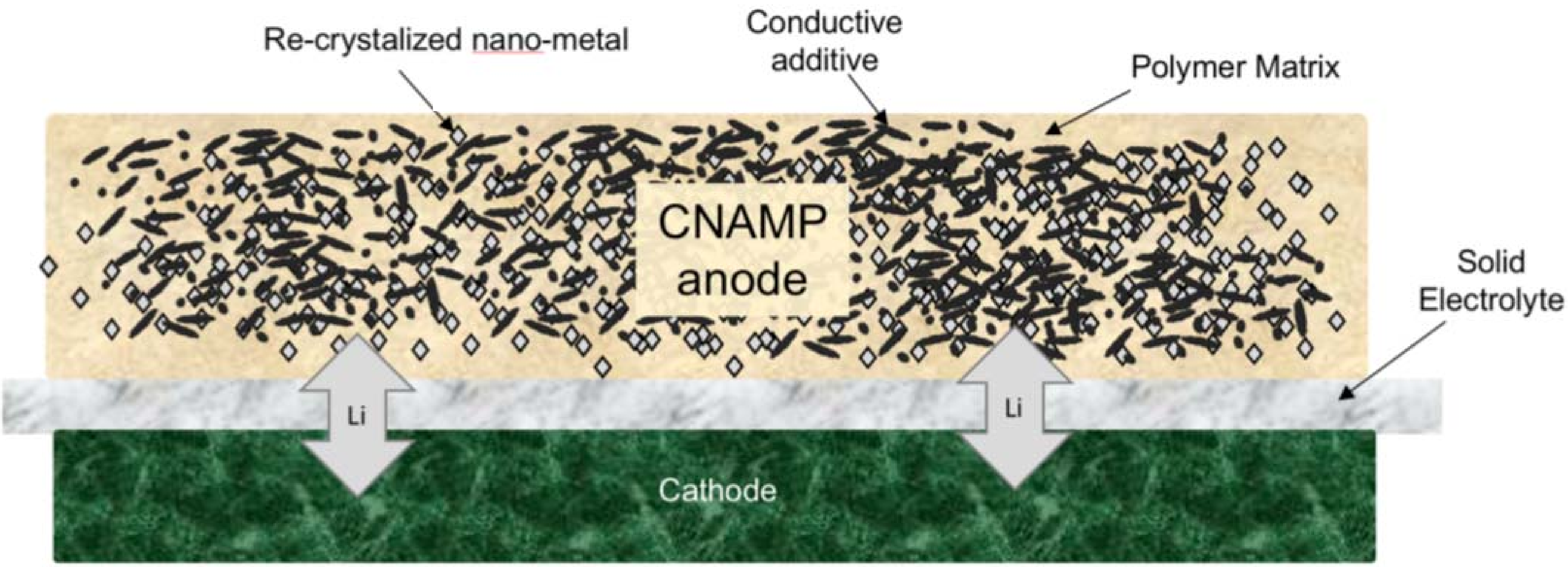
# Anodic Interface: Poor Contact with Hard Li Metal

Contact between solid electrolytes and lithium is usually poor

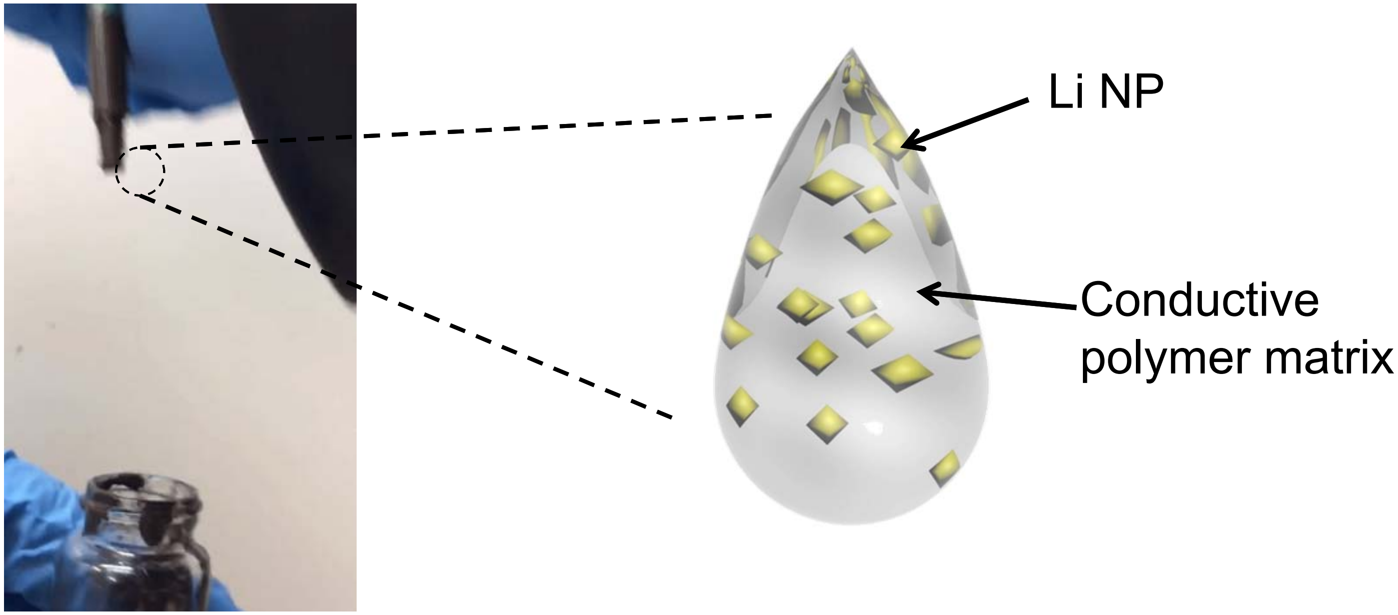


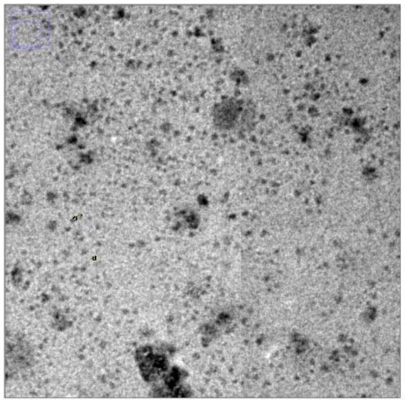
*Cui. Y., et al, Sci. Adv. 2017, 3, eaao0713*

To solve
the contact problem

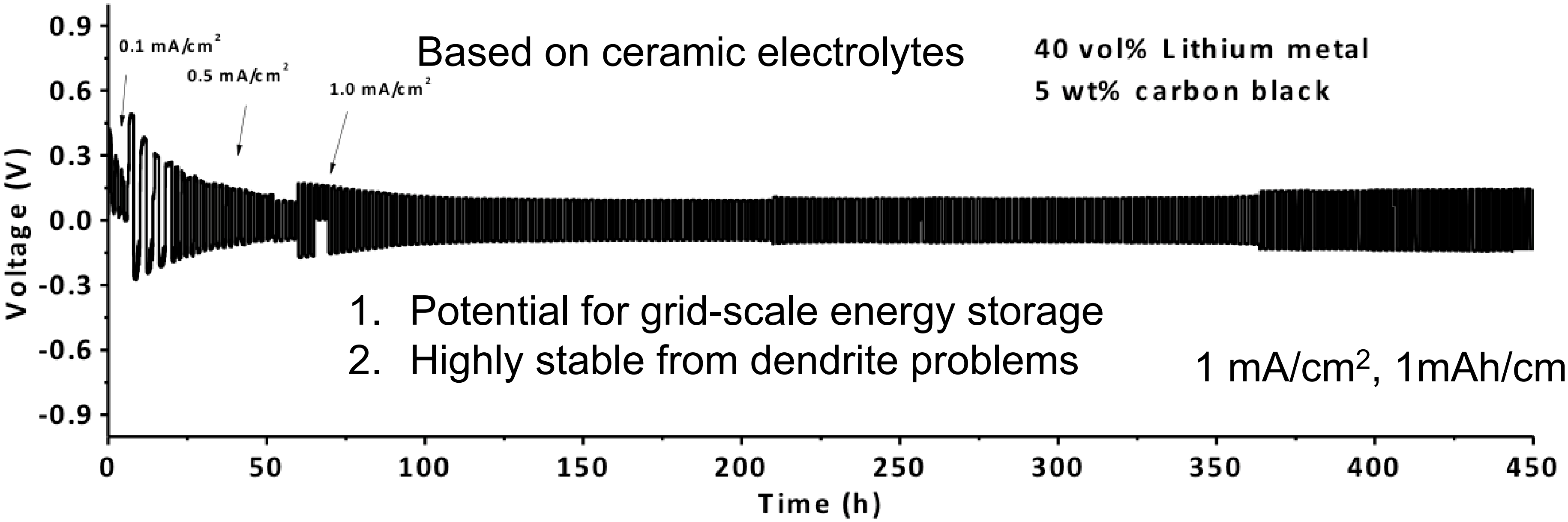


# Liquid-Like Li Metal Anode





50x50 micron



Based on ceramic electrolytes

1. Potential for grid-scale energy storage
2. Highly stable from dendrite problems

1 mA/cm$^2$, 1mAh/cm$^2$

# Outlook: Advanced Polymers in Li-Based Batteries

1. Improve safety issues of both Lithium-based battery

*A commercial solid polymer electrolytes, Conductivity: 1 x $10^{-4}$ S/cm at r.t.*

*www.ionicmaterials.com*

2. Realize grid-scale energy storage using Lithium-based battery technology

*Much higher energy capacity compared to current flow battery*

# Macromolecular Engineering

Edited by Krzysztof Matyjaszewski,
Yves Gnanou, Ludwik Leibler

WILEY-VCH

**Macromolecular Engineering**

Precise Synthesis, Materials Properties, Applications

**Volume 1:** Synthetic Techniques

Macromolecular Engineering:
Rational Design, Synthesis & Processing to
Efficiently Make Targeted Functional Materials

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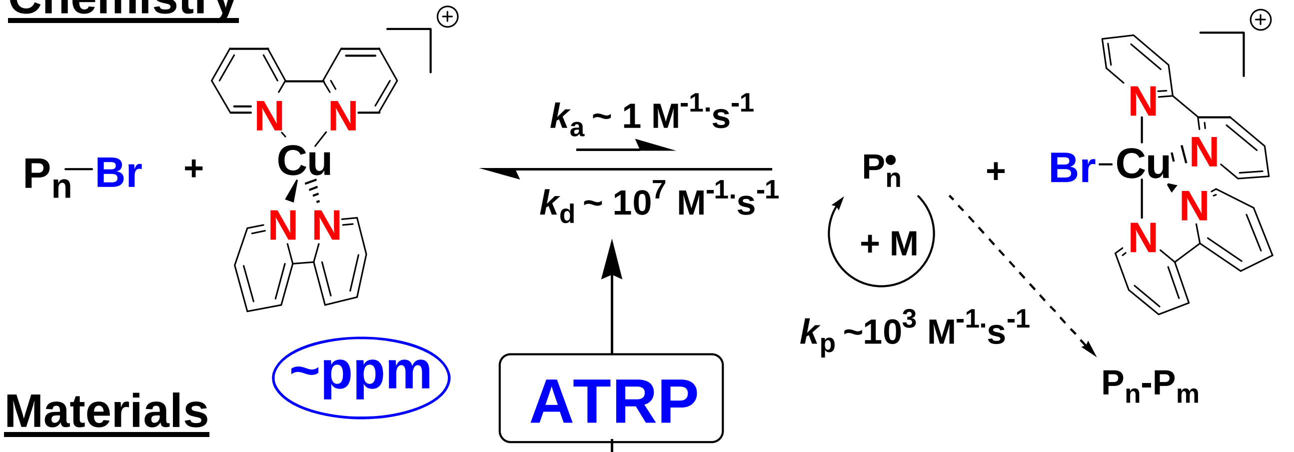
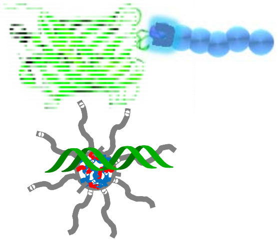
***-Polymeric Drugs***
***-Biomineralization & Double Hydrophilic Polymers***
***-Polymeric Bioconjugates***
***-Gels***
***-Tissue Engineering***

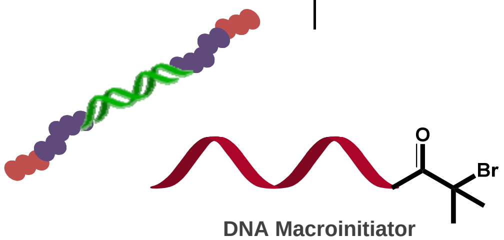
# Macromolecular Engineering
## by Taming Free Radicals

### Chemistry

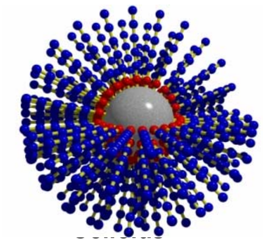


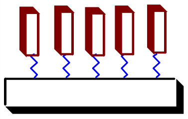
### Materials





DNA Macroinitiator

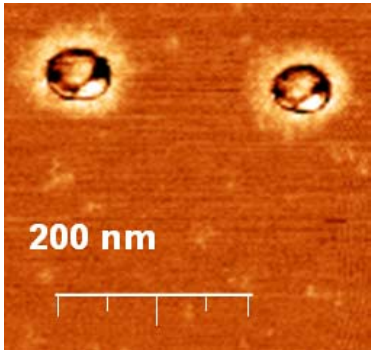


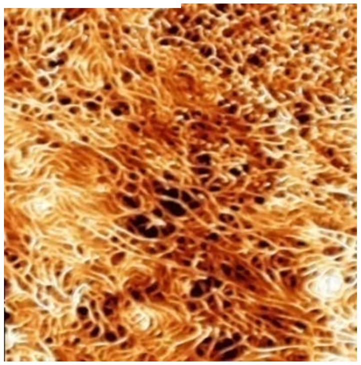

Modified Surfaces

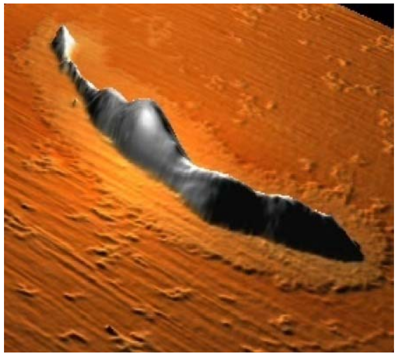
Cu-mediated redox process:
-1,000,000,000 times increased activity (=> ppm Cu & environmentally benign reducing agents: Vitamin C, sugars, iron, electrical current, light)
-Solventless or water based media

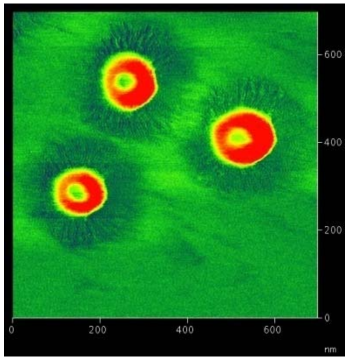
Nanostructured materials:
-controlled complex architecture
-hybrids and bioconjugates

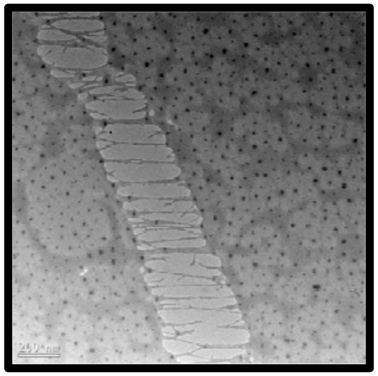
Applications (16 industrial licenses):
-coatings, adhesives ,surfactants, additives, dispersants, lubricants, gels, thermoplastic elastomers, sealants, health & beauty products, nanocomposites, hybrids, electronics, biomaterials…











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