Functional Polymers – Building Blocks for Macromolecular and Supramolecular Architectures

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Nanostructured materials with controlled architectures and responsive surfaces

Building blocks

- block and graft copolymers
- micelles of micro- and macromolecular compounds
- functional polymers
- conjugated polymers
- supramolecular structures
- liquid crystalline polymers
- coordination polymers
- hybrid organic/inorganic structures
- micro- and nanoparticles
- biomacromolecules

Micro- and nanoparticles

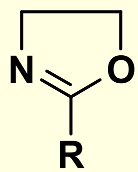
- perfect spherical shape
- extremely uniform size distribution
- accurately controlled diameter
- well-characterized surface (functionality, morphology)
- controlled porosity
- various physical properties

> **large variety**
> **high surface area**
> **controlled inner reactivity**

Topics

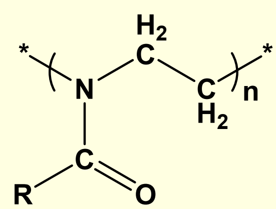
- **Poly[(N-acylimino)ethylene] (PNAI) building blocks**
  - **Functional micro- and nanoparticles based on PNAI building blocks**
  - **PNAI – based gels**
- **Functional siloxane building blocks**
  - **Poly(ε-caprolactone) – polydimethylsiloxane di- and triblock copolymers (PεCL–PDMS)**
  - **PDMS with end or pendant pyrrolyl groups**
- **Polyrotaxanes**
- **Conclusions**

Poly[(N-acylimino)ethylenes] (PNAI)

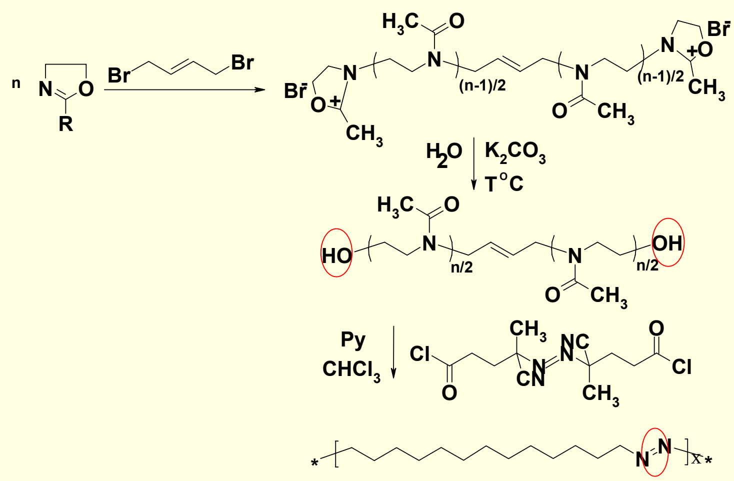


- ✓control of structural properties (living cationic polymerization)
- ✓biocompatibility or no acute toxicity
- ✓hydrophilic or hydrophobic properties (R)
- ✓chelating ability
- ✓good adhesion to polar surfaces
- ✓facile modification to PEI
- ✓compatibility with most common organic polymers
- ✓chain flexibility
- ✓crystallization ability

tailored polymers
multifunctional polymers
complex architectures

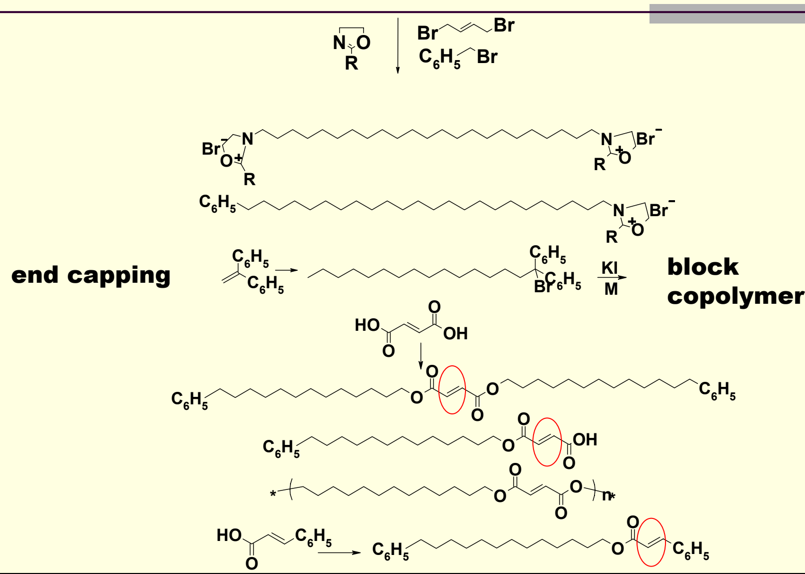


Poly[(N-acylimino)ethylene] azo initiators



PNAI azo initiator

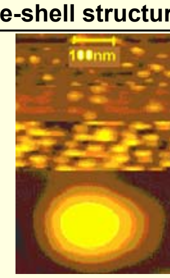
Functional polymers by end capping of living PNAI chains



Functional micro- and nanoparticles

- dispersion polymerization
- monomer: styrene
- stabilizer: poly(N-acetylethylenimine) macromonomer
(Dn = 0.5 - 1 μm, PI = 1.02 - 1.05)

Dn: 10 – 1000 nm
PI: 1.006 – 1.2
core-shell structure

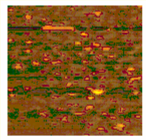
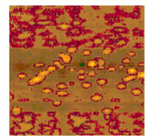
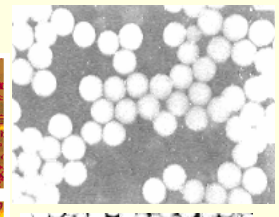
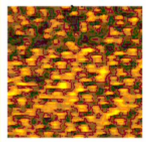
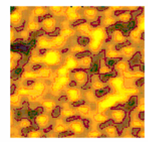
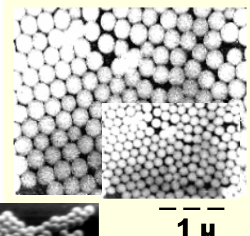


- soapless emulsion polymerization
- monomer: styrene, methyl methacrylate
- poly(N-acetylethylenimine) macroazoinitiator
(Dn = 100 - 200 nm, PI = 1.02 - 1.04)
- monomer: styrene
- poly(N-acetylethylenimine) macromonomer
(Dn ~ 200 nm, PI = 1.006 - 1.04)

- microemulsion polymerization
- monomer: methyl methacrylate, butyl methacrylate
- co-surfactant: poly(N-acetylethylenimine) macroazoinitiator or macromer
- main surfactant: SDS
(Dn = 10 - 50 nm, PI = 1.2)

Core-shell nano/micro particles by soapless emulsion polymerization

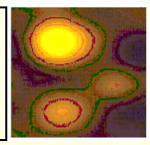
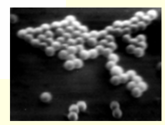
- ✓ size control
- ✓ high surface functionality
- ✓ high purity ("clean" particles)
- ✓ low toxicity
- ✓ bio-compound immobilization ability
- ✓ film forming ability
- ✓ narrow size distribution or "monodispersity"

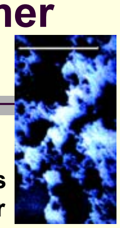
drug release systems

uniform thin polymer films (electrode coating, biosensors)

high selectivity membranes

Stable hybrid Pt nanocatalyst/polymer systems



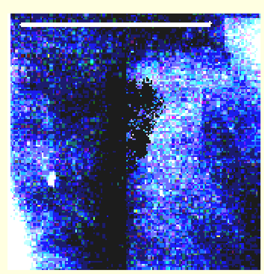
Pt catalysts

PSt - hydrolysed PNAl latex

colloidal Pt nanocatalyst particles protected by PSt-g-PNAl copolymer

retention > 90% at
136.8 µg Pt / mL
(60 min reflux)

agglomeration prevented
polymer protected
improved stability - recoverable



Pt (IV) - sorbent

maximum Pt (IV) recovery yield - in buffer solutions of pH = 10
sorption half time: $t_{1/2} \approx 90$ min
sorption capacity: 1111 µg / g latex

stable until 228 µg Pt / mL

Organic – inorganic composite materials

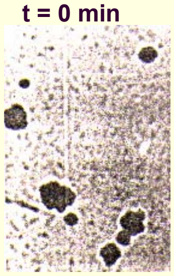
MMA polymerization in the presence of silica and PNAI macroinitiator (soapless emulsion polymerization)

Peculiarities

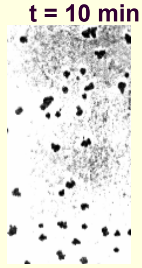
- early formed amphiphilic oligomers act as dispersants
- increased polymerization rate
- increased adhesivity to inorganic particles

  water–soluble PMMA-b-PNAI ⟶ dispersant

t = 0 min



t = 10 min



⟶ homogeneous composite material

(t = 50 min)
PI = ~ 1.0
Dw = ~ 500 nm

PNAI – based gels

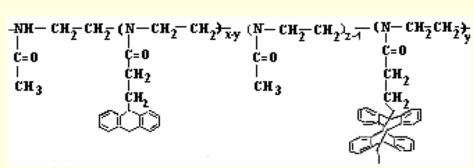
- PROZO modification followed by a crosslinking reaction of the functional prepolymers with polyfunctional compounds

  M. Heskins and J. E. Guillet, 1968
  M. Hahn, E. Görnitz, H. Dautzenberg, 1998

- random copolymerization of 2-substituted-2-oxazoline with bisoxazoline monomers

  S. Kobayashi et al., 1990
  T. Saegusa et al., 1990 -1993

- specific reactions of functionalized PROZO: photodimerization of the photosensitive pendant groups or coordination of the metal ions to reactive inserted groups

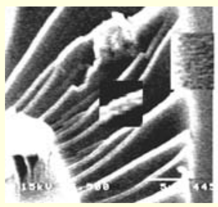


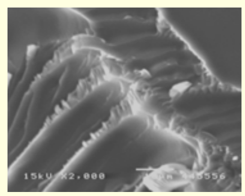
- copolymerization of ROZO and bisoxazoline with special "macroinitiator"

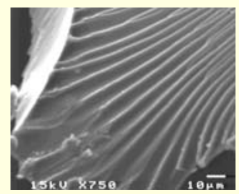
  J. Rueda and B. Voit, 2003

Thermosensitive gels

Precipitation polymerization
Monomers: HEMA
NIPAAm (LCST 32°C)
PNAl macromonomers (PEOZO – LCST 36°C)
Reaction conditions: HEMA/NIPAAm/PROZO w/w/w - 1:1:1
60°C, ethanol, AIBN, Ar, 20h







self assembled core-shell microparticles
interconnected pore structure

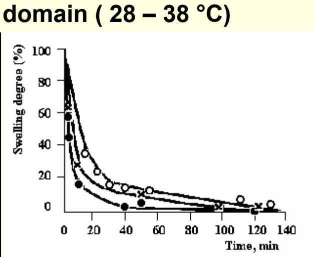
large channels
open macropores

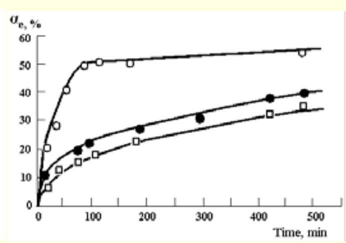
Stimuli responsive hydrogels
(temperature responsive)

controlled structure and characteristics (hydrophilic/hydrophobic balance, crosslinking density, amount of thermosensitive chains)

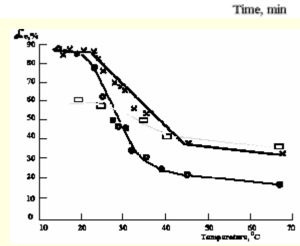
LCST – therapeutic domain (28 – 38 °C)

Sample	LCST (°C)
M_6	27.5
M_{15}	32.0
M_{25}	33.0
M_{45}	38.0
E_{15}	28.5
E_{25}	30.0
E_{35}	32.0
E_{45}	31.5
BC_1	28.5
BC_2	27.6

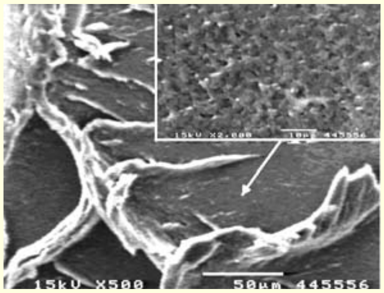




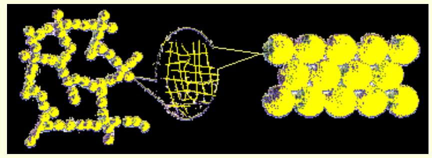
Swelling/deswelling kinetics



Self-assembling microgels



PEOZO/PNIPAAm/PHEMA hydrogel



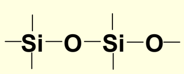
Self-assembling network
(ordered or not ordered)

Microgels

Thermosensitive gels

“on-off” switching materials
controlled drug delivery and storage systems
biomacromolecules storage/release
tissue engineering, in combination with biodegradable polymers (collagen)

Siloxane building blocks



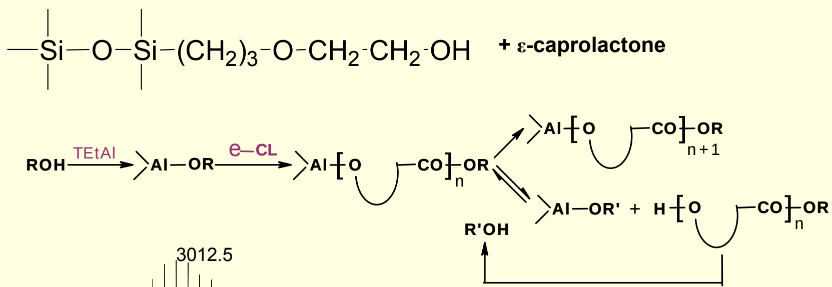
- ✓ hybrid organic - inorganic polymers
- ✓ biocompatibility (physiological inertness)
- ✓ high gas permeability
- ✓ good oxidative, thermal and UV stability
- ✓ high chain flexibility
- ✓ very low solubility parameter and low surface tension (immiscibility with most organic polymers)

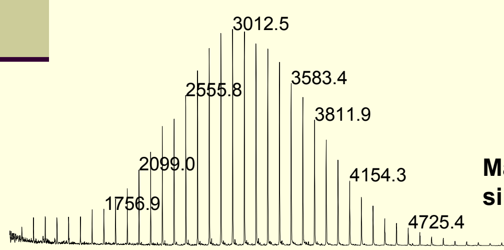
Functional siloxanes and siloxane copolymers

- ➢ blend compatibilizers
- ➢ surface modifiers
- ➢ biomaterials (contact lenses, implants, transdermal penetration enhancers)

Poly(ε-caprolactone) – polydimethylsiloxane di- and triblock copolymers

Controlled coordinating anionic polymerization

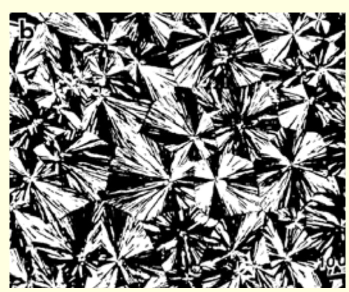




Maldi Tof spectra of caprolactone – siloxane copolymers

PεCL - PDMS copolymer morphology
(polarized optical microscopy)

CL_{2000}-SiO_{1000}-CL_{2000}



CL_{6000}-SiO_{1000}-CL_{6000}

Poly(ε-caprolactone) – polydimethylsiloxane di- and triblock copolymers

Poly(ε-caprolactone)

- ✓ biocomatible and biodegradable
- ✓ relatively hydrophobic
- ✓ high cristallinity

- ✓ vehicles for the slow release of drugs
- ✓ biodegradable and biocompatible ceramers for the repair of skeletal tissues

PεCL-PSi nanoparticles loaded with IMC and VE

❑ Unloaded particles

Size: 124 – 194 nm

Distribution width: 0.07 – 0.15

❑ Loaded particles

✓ IMC

Size: 130 – 194 nm

Distribution width: 0.11 – 0.18

✓ VE

Size: 249 – 350 nm

Distribution width: 0.43 – 0.57

❑ Drug loading efficiency (%)

✓ IMC 10.05 – 12.80

✓ VE 52.80 – 54.75

Conducting polymers in rotaxane structures

Polyrotaxanes – supramolecular inclusion complexes composed of macrocycles (host molecules) threaded onto linear macromolecules (guests)

Conducting polymers

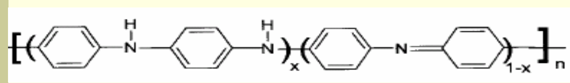
- rigid structures
- low molecular weights
- insoluble, not meltable, difficult to process

Rotaxane structures

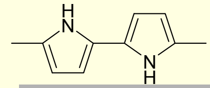
- increased solubility
- superior balance of physical properties and processing capabilities
- diminished aggregation or concentration quenching by maintaining the co-facial π-systems at the fixed minimum separation determined by the thickness of macrocycle walls

- photo- and electro-active devices
- catalysis
- membranes for mass transfer

Polyaniline



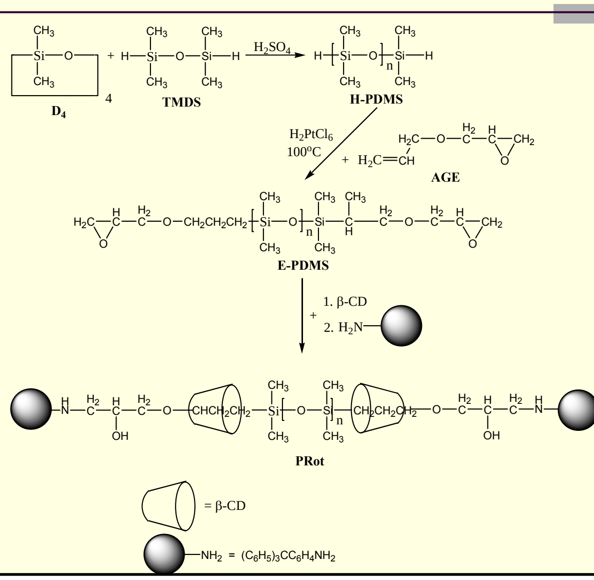
Polypyrrole



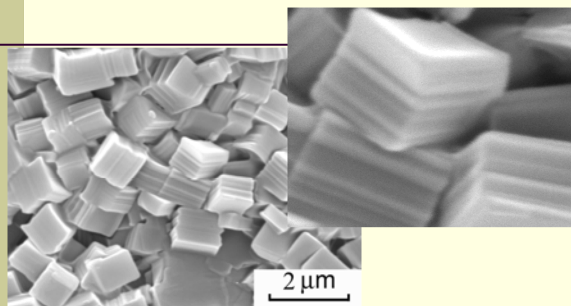
POLYMER	CONDUCTIVITY (S/cm)*	SOLUBILITY (DMF)**
Polyaniline	**4.5 x 10^{-2}**	**(-)**
Polyaniline / αCD	**8.4 x 10^{-4}**	**(+)**
Polyaniline / βCD	**1.8 x 10^{-3}**	**(+)**
Polypyrrole	**6.1 x 10^{-3}**	**(-)**
Polypyrrole / αCD	**4.8 x 10^{-4}**	**(+)**
Polypyrrole / βCD	**5.2 x 10^{-3}**	**(+)**

*** after dopping with iodine**
**** (-), insoluble; (+), soluble**

β-cyclodextrin – polydimethylsiloxane polyrotaxanes

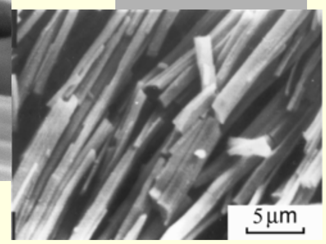


β-cyclodextrin – polydimethylsiloxane polyrotaxanes



Epoxy-terminated PDMS – β CD + free β CD

- ✓ perfect parallelepipeds
- ✓ mean edge size of parallelepipeds – 0.81 µm
- ✓ each crystal consists of stacked lamellae
- ✓ mean lamellae width – 0.1 µm

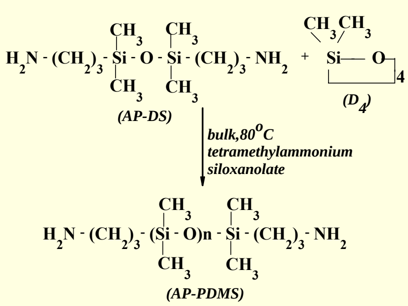


Epoxy-terminated PDMS – β CD

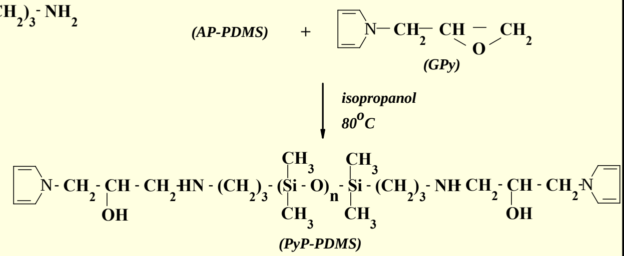
- ✓ long rod-like crystals
- ✓ mean thickness of the crystals – the same value as the mean lamellae size

Pyrrolyl terminated PDMS

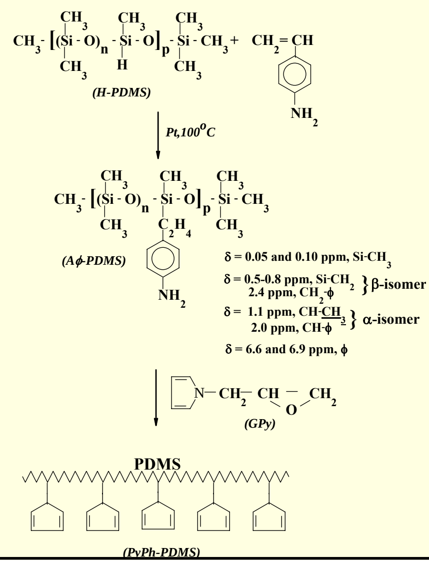
Equilibration of D4 with AP-DS



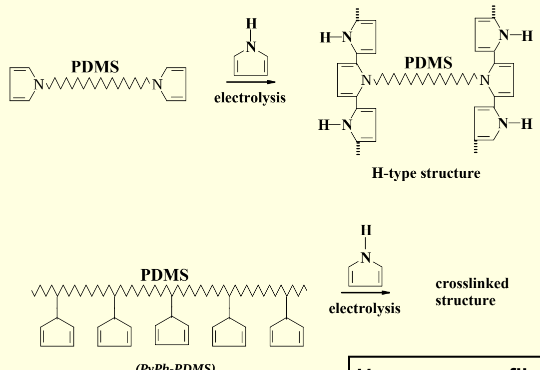
Coupling of AP-PDMS with GPy



PDMS with pendant pyrrolyl groups



Electrocopolymerization of pyrrole with pyrrolyl functionalized PDMS



Homogeneous **films with** *good mechanical properties* **and** *phase separated morphologies*
Thermal transitions **and** *thermal stability* **depend on dopant nature**
Conductivities: **2 - 5 S/cm, independent on dopant nature**

Conclusions

Functional polymers (oligomers) – versatile intermediates (building blocks) for complex, nanostructured architectures and new polymeric materials

- **core-shell nano- and microparticles**
- **porous microparticles**
- **thermosensitive gels (hydrogels)**
- **organic – inorganic composite materials**
- **controlled drug delivery systems**
- **semi-conducting polymer films**
- **hybrid nanocatalyst/polymer systems**
- **supramolecular inclusion complexes (polyrotaxanes)**

Thank you for your attention!