Polymers in Solution

Dresden, 19th October 2022

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Polymers in solution: Planification

Winter Semester

- 12th October (missing)
- 19th October
- 26th October
- 2nd November
- 9th November
- 16th November → Day off
- 23rd November
- 30th December
- 7th December

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- 14th December
- 22th December
- 4th January
- 11th January
- 18th January
- 25th January
- 1st February

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Exam??? One week after

Responsible: **Prof. Dr. Albena Lederer** lederer@ipfdd.de

Polymers in solution: Planification

1. **Introduction and classification of macromolecular structure. Applications**
2. **The isolated macromolecule**
3. **Block Copolymers in solution. Macromolecular Self-Assembly**
4. **Thermodynamics of polymer solution and blends**
5. **The statistical character of macromolecules**
6. **Molar mass determination, colligative properties**
7. Static light scattering
8. Dynamic light scattering
9. Solution viscosity
10. Scaling and molar mass dependent parameters
11. Polymer separation
12. Branching and cross-linking

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Please go to my Homepage Lectures

Introduction and classification of macromolecular structure. Applications

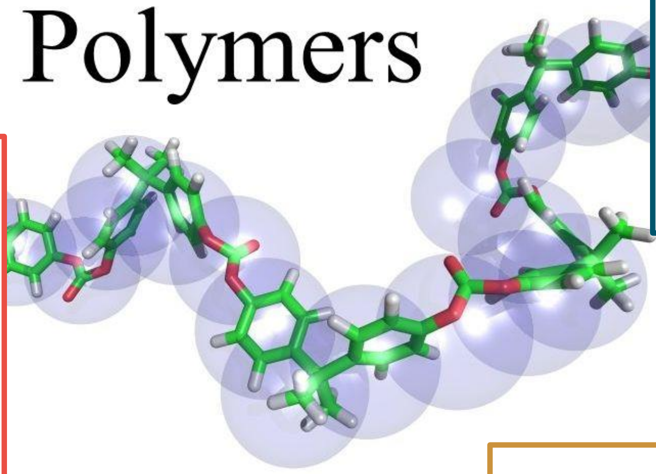
1. General classification
2. How to control (fine tune) the properties
3. Characterization methods
4. Physico-chemical characterization of biohybrid polymer compartments
5. Mimicking biological functionality with polymers for biomedical applications
6. Smart Polymers. Applications

1. General classification

A. Based on origin of source

Natural polymers

Synthetic polymers



B. Based on structure/Topology

Linear polymers

Branched chain polymers

Cross-linked polymers

C. Based on molecular forces

Elastomers

Fibers

Thermoplastics

Thermosetting polymers

D. Based on mode of polymerization

Addition polymers

Condensation polymers

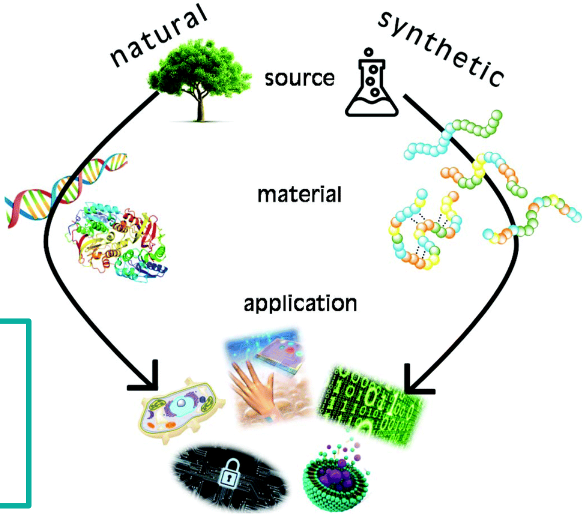
A. Natural polymers and synthetic polymers → Based on origin of source

Natural Polymers	Synthetic Polymers
They are found **naturally** in our enviroment (human body, animals, plants…)	They are produced **artificially** by humans
They occur naturally	Do not occur naturally
They are produced from **biological processes**	They are produced from **chemical processes**
Most polymers are **easily degradable** by biological process	Most polymers are **hard to degrade** by natural process
They are readily accepted by the body and possess **high bioactivity and biocompatibility**	They often lack much-desired bioactivity and biocompatibility → **adverse side effects**

Synthetic + natural based biodegradable polymers have received much more attention in the last decades → potential applications in the fields related to environmental protection and the maintenance of physical health

Semi-synthetic polymers → cellulose derivatives

cellulose acetate (Rayon)

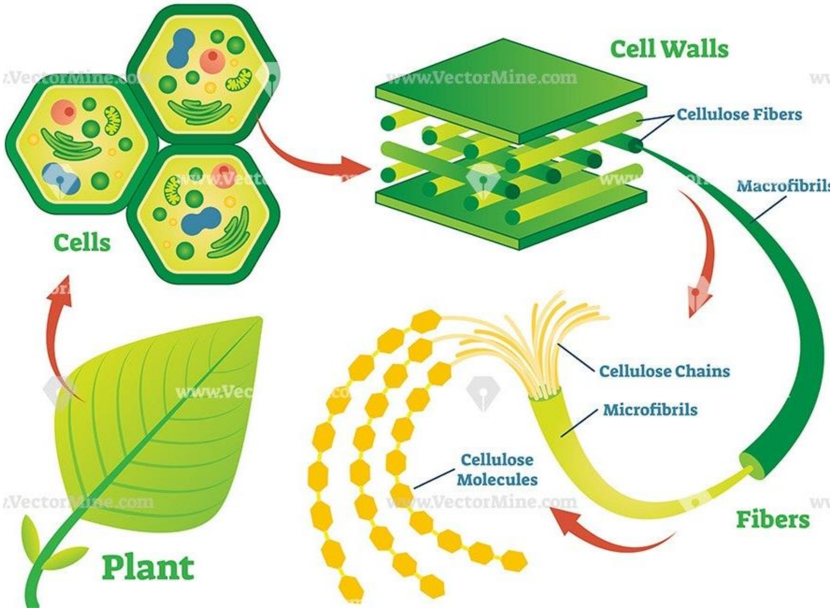


Natural polymers and synthetic polymers → Based on origin of source

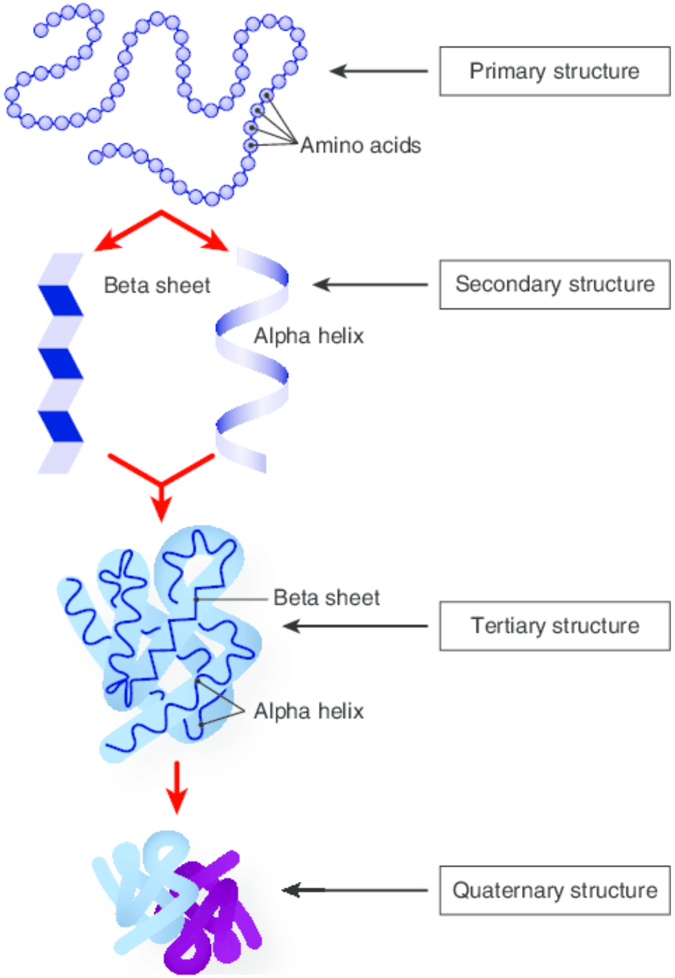
Examples Natural polymers

a) Polysaccharides

Hyaluronic acid (HA), chondroitin sulfate, chitin and chitosan, alginates and cellulose.



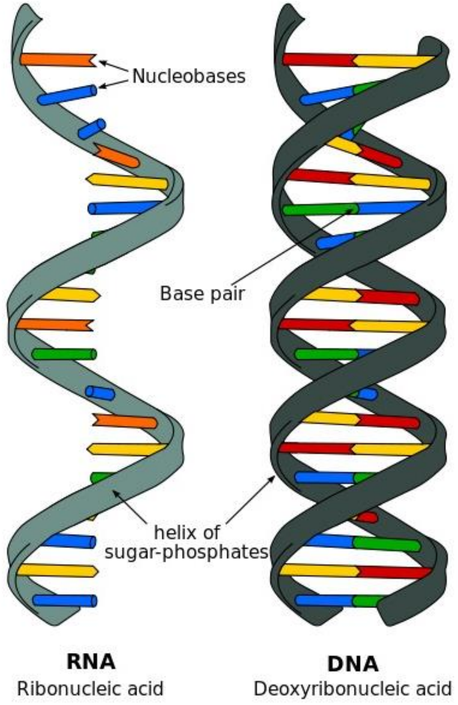
b) *Proteins*



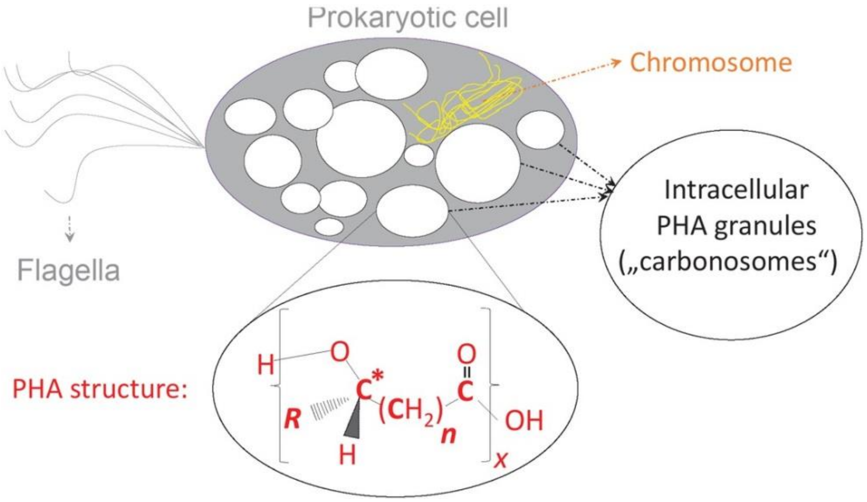
Natural polymers and synthetic polymers ➔ Based on origin of source

Examples Natural polymers

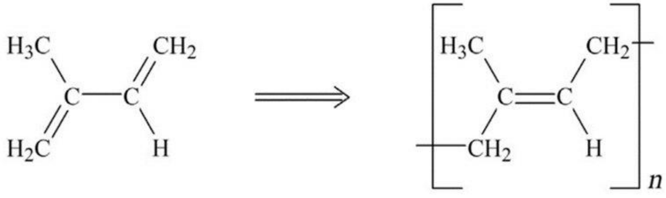
c) Polynucleotides (DNA or RNA)



d) *Polyesters*



Poly-3-hydroxybutyrate (P3HB) production by bacteria

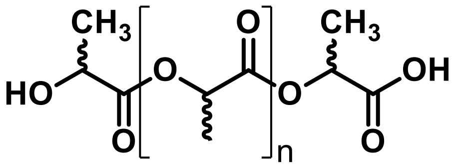


Isoprene

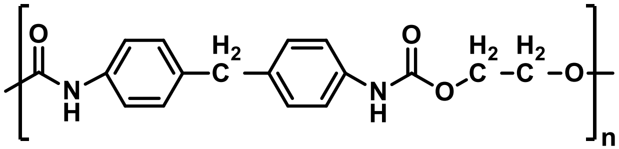
Natural rubber (polyisoprene)

Natural polymers and synthetic polymers ➔ Based on origin of source

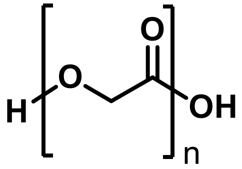
Examples Synthetic polymers



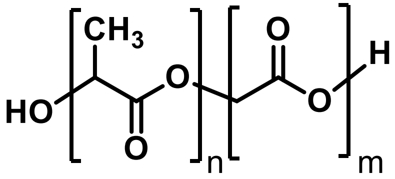
Poly Lactic Acid (PLA)



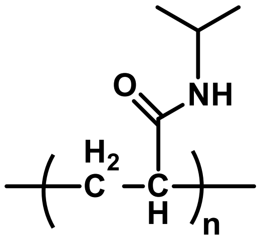
Polyurethane (PU)



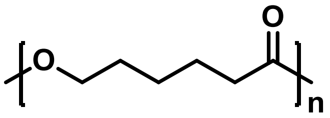
Poly(glycolic acid) (PGA)



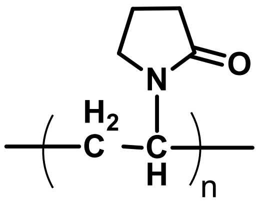
Poly(lactic-co-glycolic acid) (PLGA)



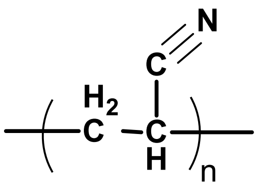
Poly(N-isopropylacrylamide) (PNIPAAm)



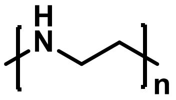
Polycaprolactone (PCL)



Poly(N-vinyl Pyrrolidone) (PVP)



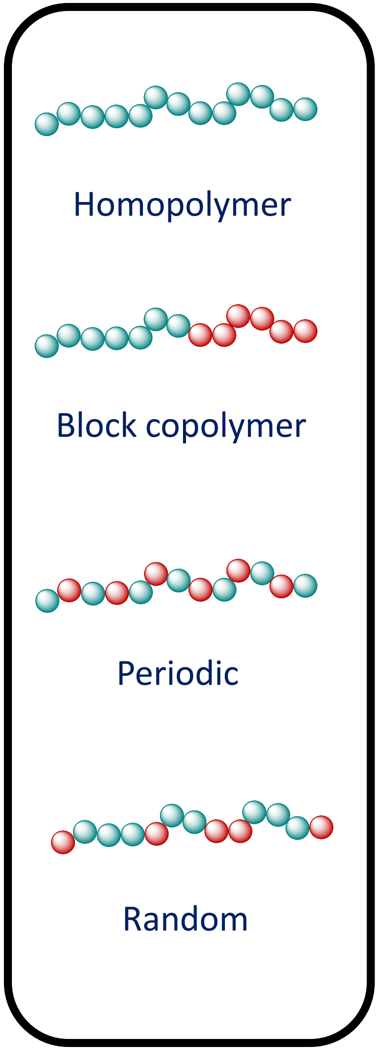
Polyacrylonitrile (PAN)



Polyethylenimine (PEI)

B. Polymers classification based on structure/Topology

a. Composition



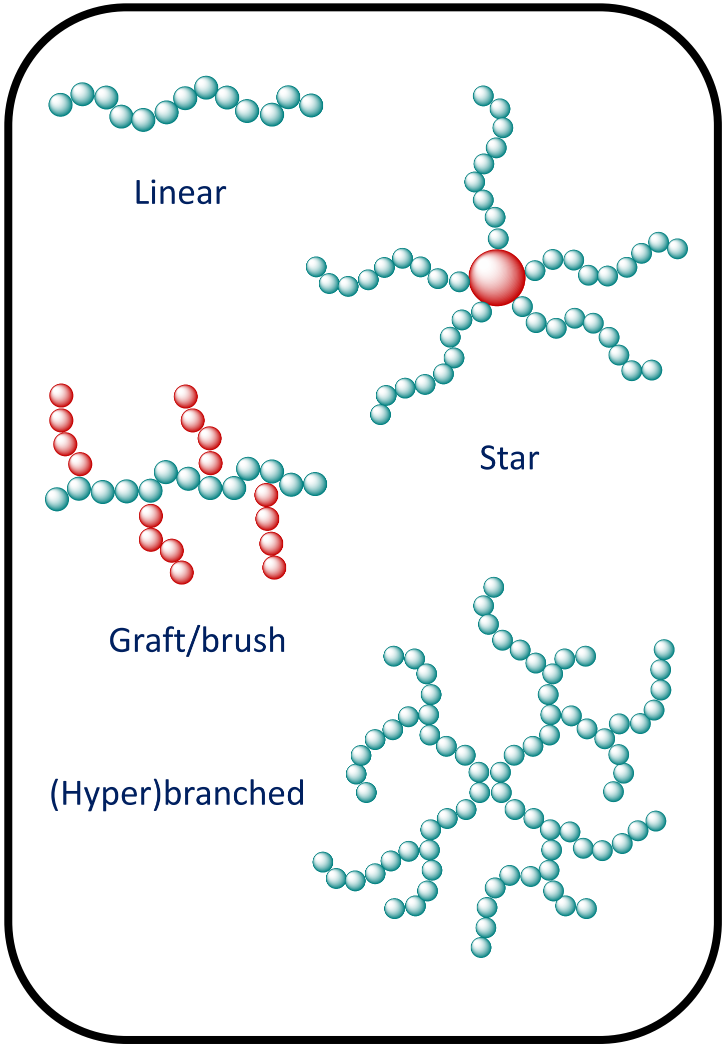
Homopolymer

Block copolymer

Periodic

Random

b. Topology



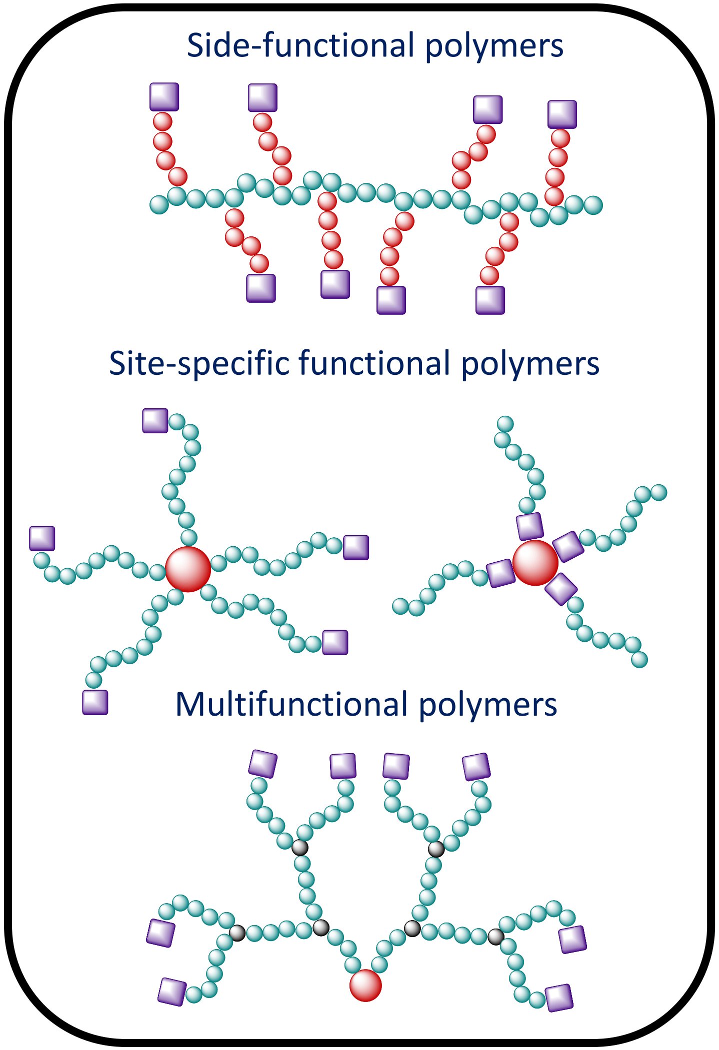
Linear

Star

Graft/brush

(Hyper)branched

c. Functionality



Side-functional polymers

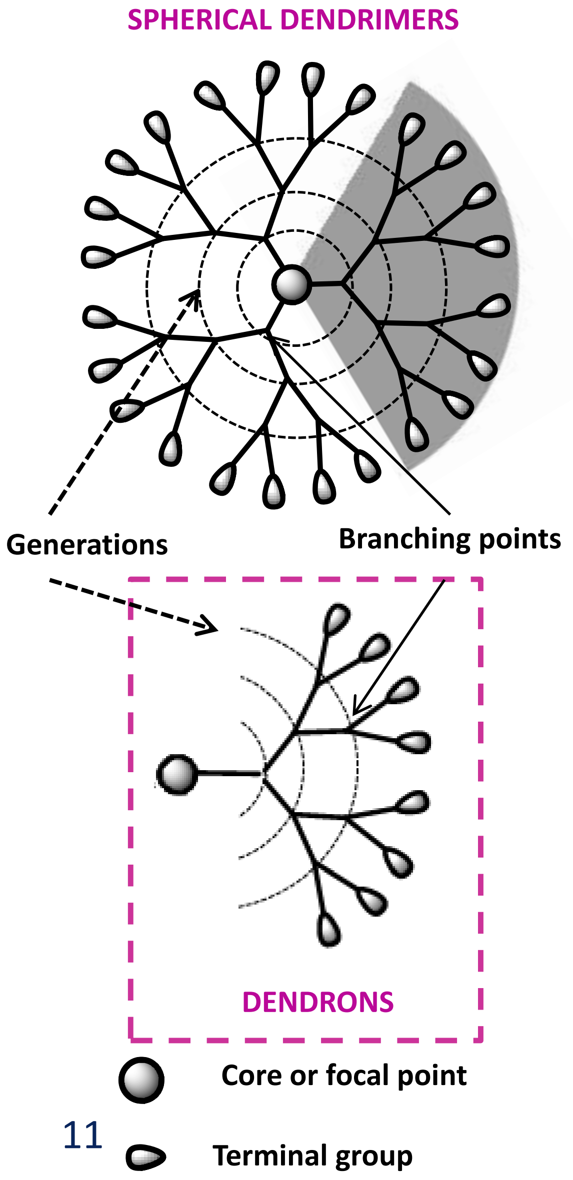
Site-specific functional polymers

Multifunctional polymers

B. Polymers classification based on structure/Topology

Dendronization of systems

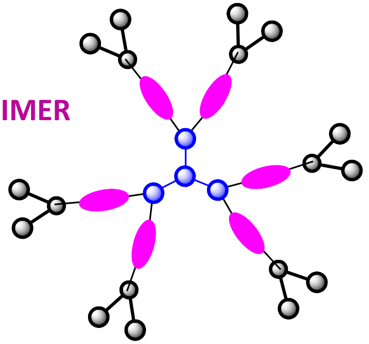
SPHERICAL DENDRIMERS

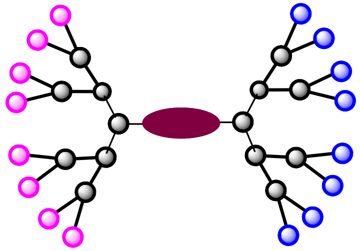


i. Dendronization of different biomolecules at the focal point (drugs, metal complex, peptides, chromophore, etc).

ii. Hybrid dendrimers, with different **building blocks** at the skeleton **("onion peel")** or **different topologies ("bow-tie", Janus).**

HYBRID DENDRIMER

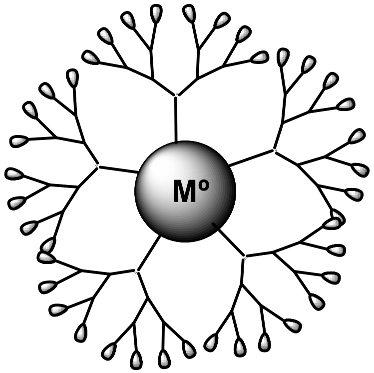


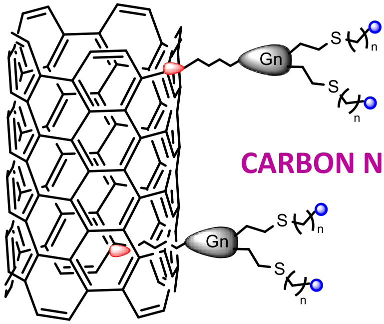


BOW-TIE "O "JANUS"

iii. Nanostructurated materials such as nanotubes or nanoparticles.

METAL NANOPARTICLES



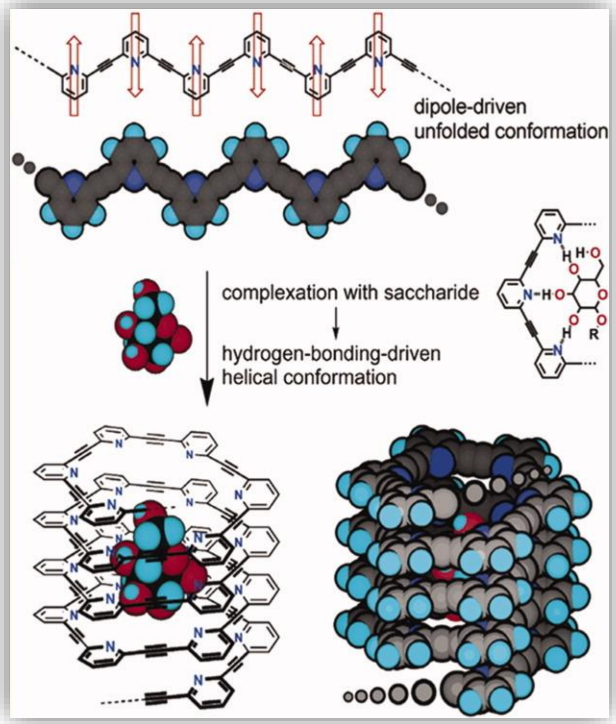


CARBON NANOTUBES

B. Polymers classification based on structure/Topology

Supramolecular

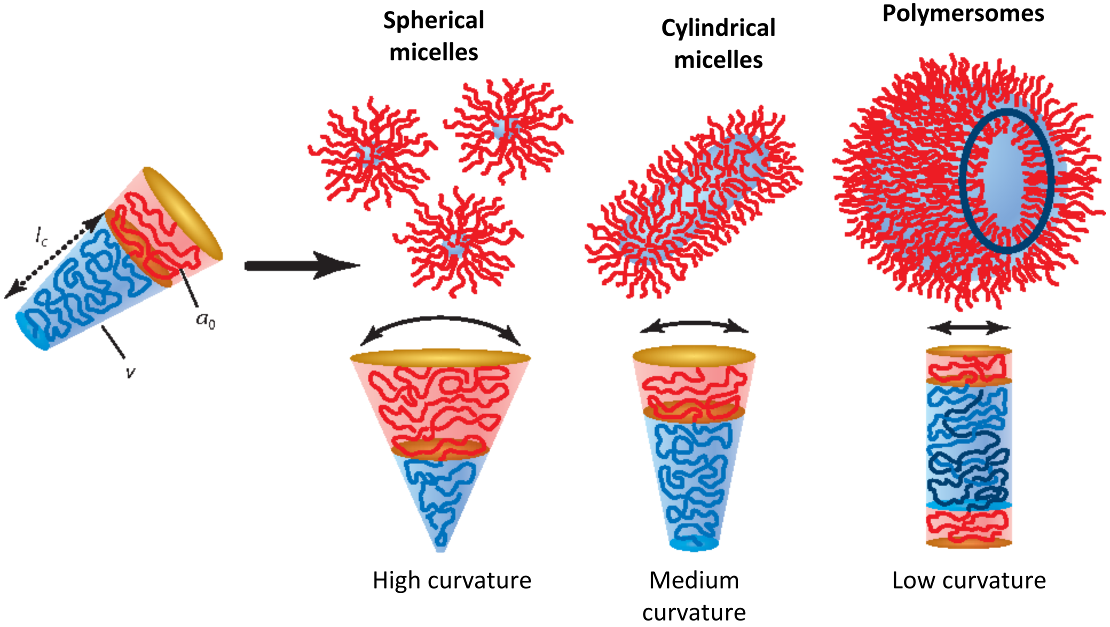
Self-assembly of supramolecular polymers into tunable helical structures



Conformational change of poly(m-ethylpyridine) driven by the compexation with saccharide.

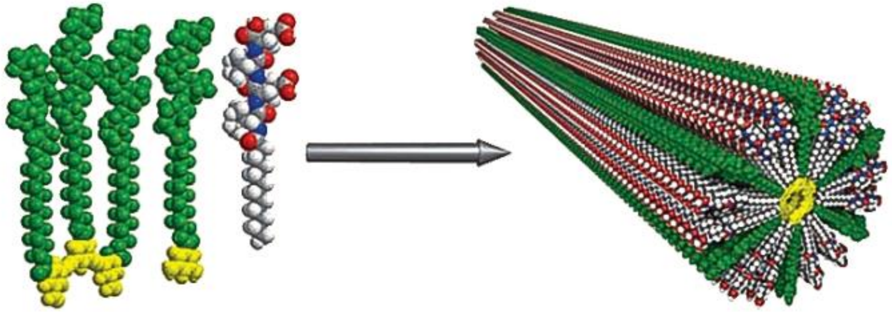
https://doi.org/10.1002/pola.22569

Self-assembly of block copolymers



10.1146/annurev-chembioeng-060713-040447

Hybrid rod-like polymers



DOI: 10.1126/science.aad4091

NEXT LECTURE

B. Polymers classification based on structure/Topology

Amphiphilic Block Copolymers (Hydrophobic and Hydrophilic Block)

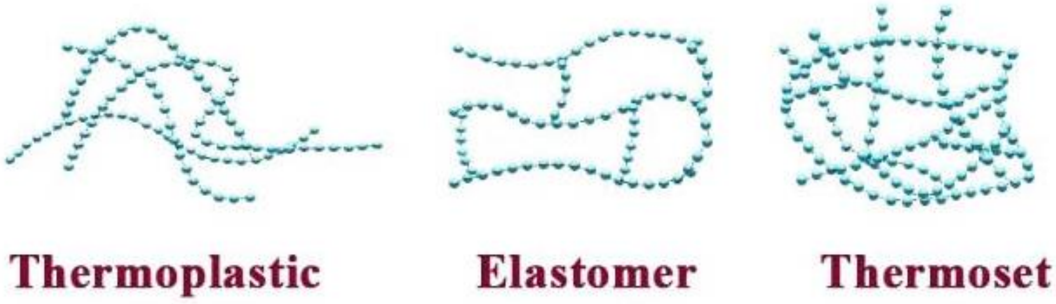
A new visible light and temperature responsive diblock copolymer

The **PmAzo-b-PNIPAM block copolymer** forms **micelles in water**: **core** → hydrophobic and visible light responsive PmAzo block; **outer** → the thermo-responsive PNIPAM block keeps the micelles suspended in water. **The PmAzo-b-PNIPAM micelles are thermo-responsive and photo-responsive.**

The visible-light-induced isomerization of the azobenzene moieties in the PmAzo block leads to a decrease or increase of the hydrodynamic diameter D_h of the micelles depending on the irradiation light wavelength.

Polym. Chem., 2019,**10**, 5001-5009

C. Polymers classification based on molecular forces



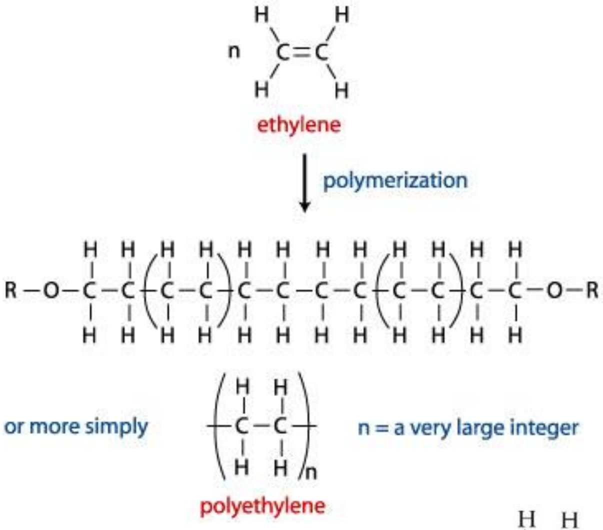
Nylon fibers are exceptionally strong and elastic and stronger than polyester fibers. The fibers have excellent toughness, abrasion resistance, and are easy to wash, and to dye in a wide range of colors. The filament yarns provide a smooth, soft, and lightweight fabric of high resilience.

Biopolymers. Polymers which are produced by or derived from living organisms. They are biodegradable and have a very well defined structure. Various biomolecules like carbohydrates and proteins are a part of the category.

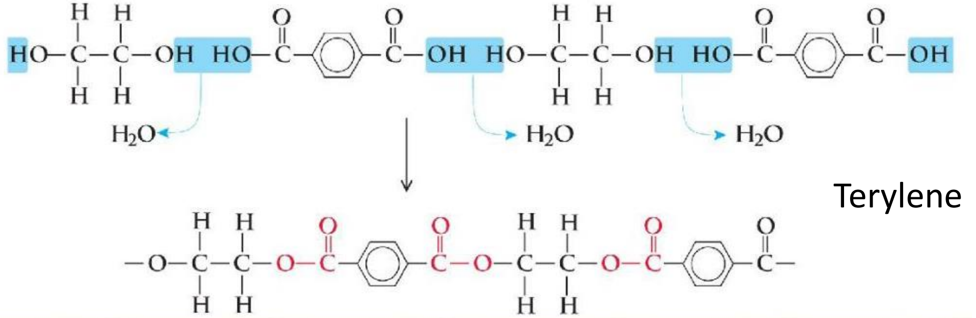
D. Polymers classification based on mode of polymerization

Clasification based on type of polymerization

Addition Polymers

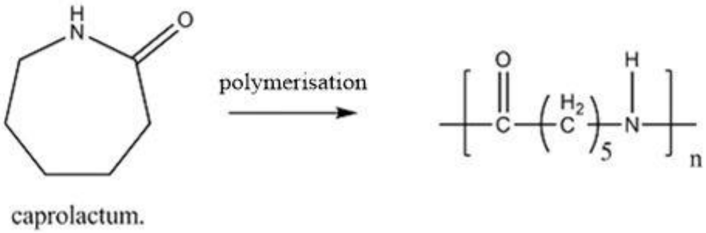


Condensation Polymers



Terylene

Ring Opening Polymers



Nylon-6

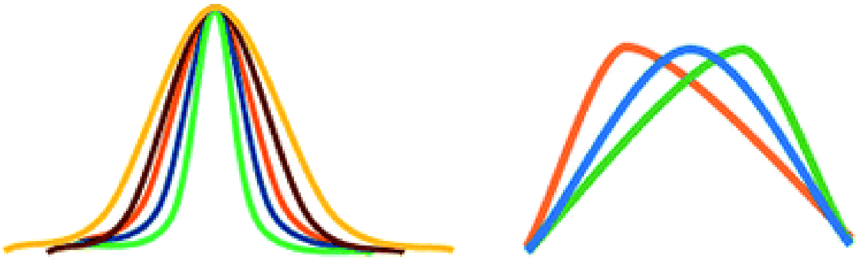
perlon

2. How to control (fine tune) the properties

1. Variation of molar mass and mass distribution

- Low molar mass (oligomere)
- High molar mass (polymers)
- Ultra high molar mass

- Narrow or broad molar mass distribution
- Monomodal-bimodal-multimodal



Dispersity

Shape

Change of material properties

Methods to tune dispersity: a) Polymer blending; b) Temporal regulation of initiation; c) Altering catalyst concentration d) Additional reagents, chain coupling or terminating agents

Applications: a) Control of physical properties; b) Self-assembly in bulk; c) Self-assembly in solution

Chem. Sci., 2019,**10**, 8724-8734

2. How to control (fine tune) the properties

2. Changes in architecture

Linear, branched, star like, crosslinked, dendritic…

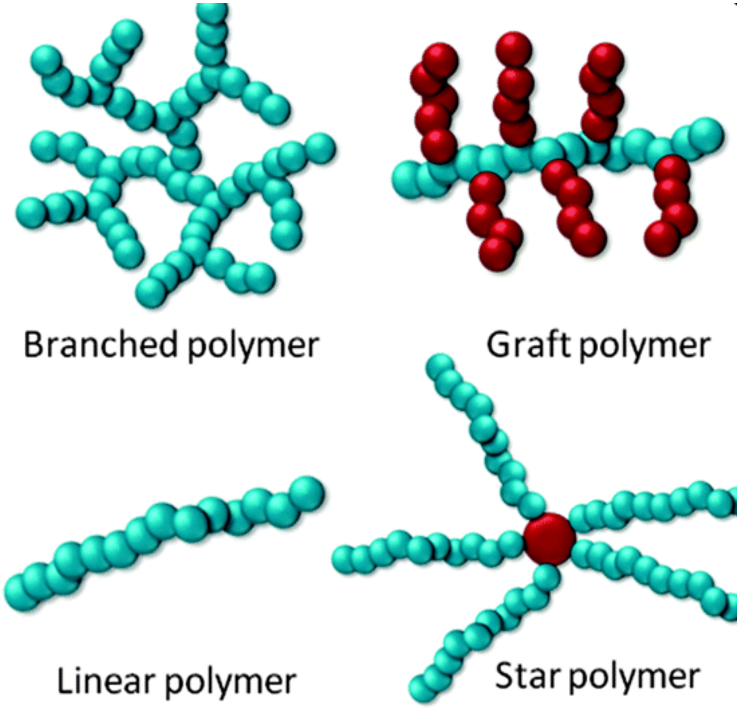
Linear: they can exist as coils or in ordered arrangement of the chain (crystallization). Disadvantage: at high molar mass ➔ high viscosity

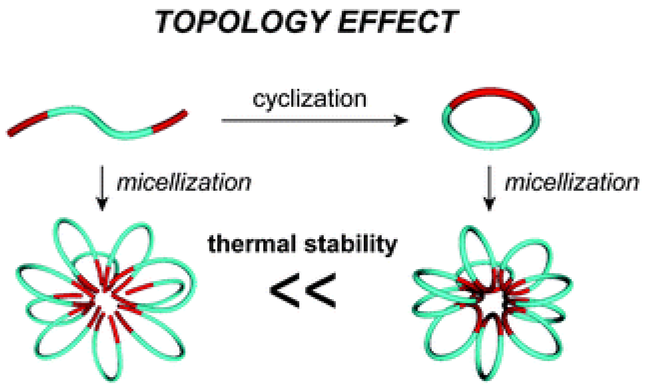
Branched: lower tendency for crystallization, lower viscosity

Star/comb: low tendency for crystallization, low dependency of viscosity on molar mass

Crosslinked: insoluble, swellable, elastic or very hard, crosslinking density can be controlled

Dendrimers: globular, high functional polymers, exact control of molar mass and dimension, specific viscosity behavior





Polym. Chem., 2011,**2**, 1930-1941

2. How to control (fine tune) the properties

3. Variations in composition

- **Homopolymers from different monomers**

Monomers and the type of polyreaction determine mainly the material properties

Olefins: aliphatic carbohydrate, ordered, high crystallinity, low solubility and thus high stability versus organic solvents, high mechanical properties, relative soft materials, limited thermal stability
Styrene: high hardness and strength, brittle; butadiene: low T_g flexible; chemical resistance, low solubility

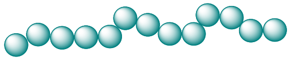
Polyesters, polyamides: exhibit H-bond -> crystallization, high mechanical strength

- Copolymers: random, alternating, blocky

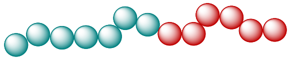
- star copolymers, graft copolymers

Copolymerization allows the combination of different repeating units and thus the combination of different properties!

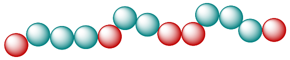
Copolymerization allows also control of architecture



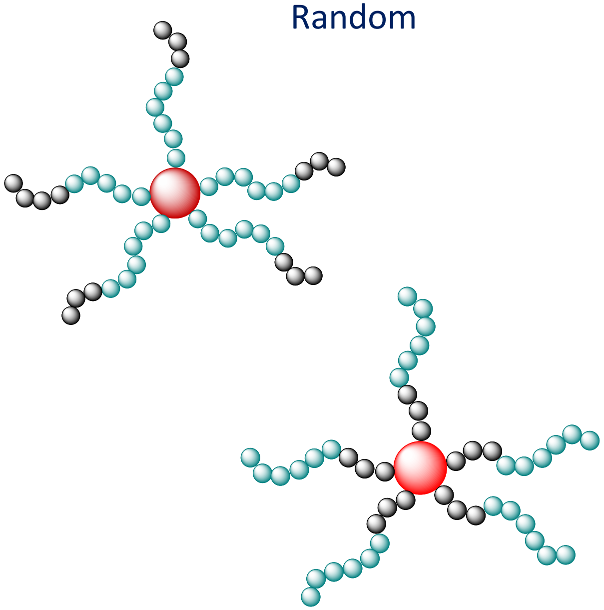
Homopolymer



Block copolymer



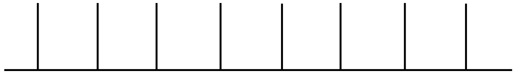
Random



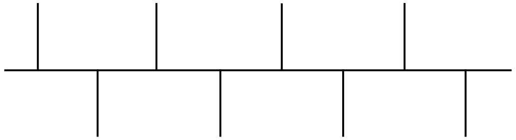
2. How to control (fine tune) the properties

4. Variations of internal structure

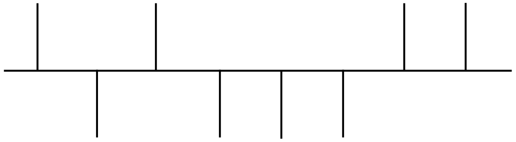
- primary structure: configuration/tacticity
- secondary structure (coil/rod)
- tertiary structure (amorphous, crystalline, partial crystalline, liquid crystalline)



Isotactic



Syndiotactic

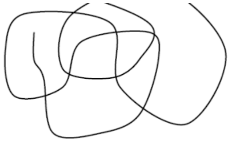


Atatic

Determine strongly thermal and

mechanical properties!

as well as optical properties!



coil
(amorphous)

worm like

rigid rod

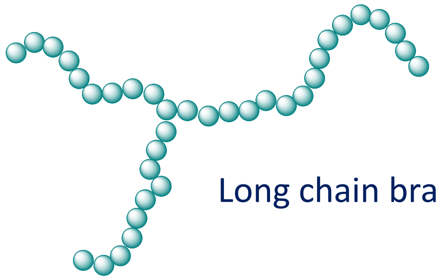
highly crystalline
sheet structure

partial crystalline
e.g. TPE

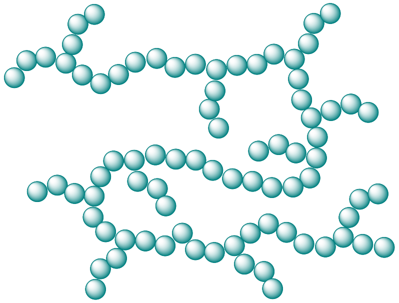
liquid crystalline
preferred orientation
of molecules or dipols

2. How to control (fine tune) the properties

5. Short and long chain branching



Long chain branching



Short chain

branching

Typical examples: polyolefins

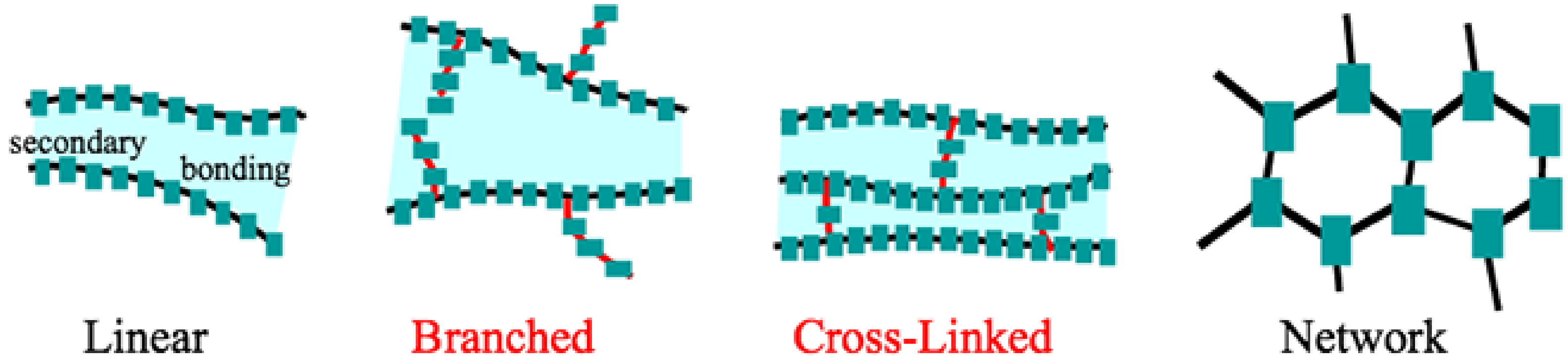
LDPE = Low Density Polyethylene
radical process, initiated with peroxides or oxygen, high pressure (1400 - 3500 bar), high temperature (150-350 °C), structure: long chain branching, low crystallinity (40-50%)

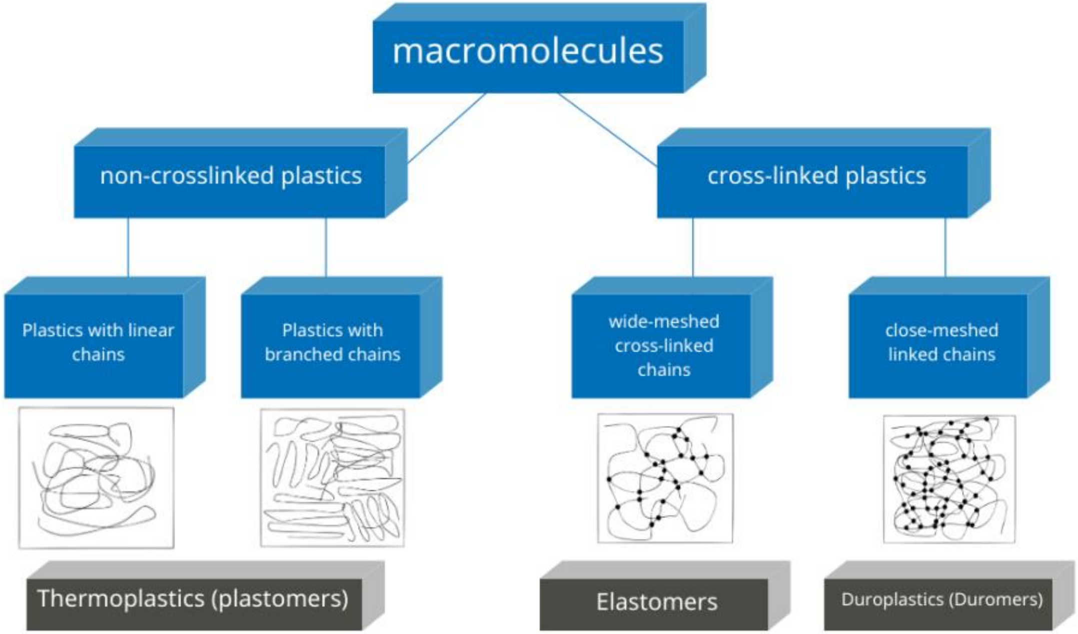
HMW-LDPE = High Molecular Weight Low Density Polyethylene
radical process, at high pressure and high temperature long chain branching, molecular weight > 200,000 g/mol

LLDPE = Linear Low Density Polyethylen, short chain branching, copolymers with 1-butene or 1-hexene Ziegler/Natta Polymerisation (heterogeneous) at low pressure long chain branching often a result of side reactions in polymerization processes

2. How to control (fine tune) the properties

5. Networks and crosslinked systems





macromolecules

non-crosslinked plastics

cross-linked plastics

Plastics with linear chains

Plastics with branched chains

wide-meshed cross-linked chains

close-meshed linked chains

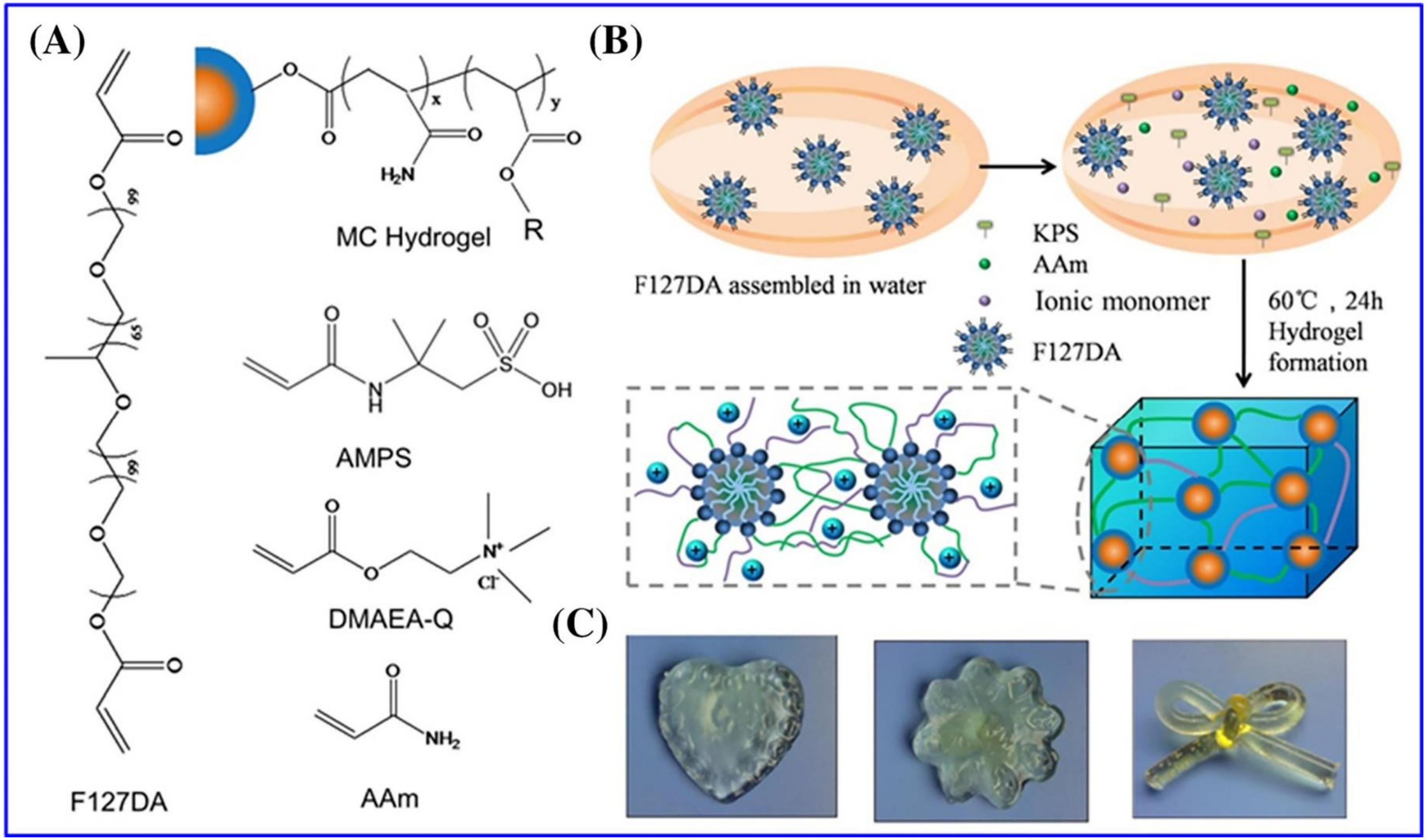
Thermoplastics (plastomers)

Elastomers

Duroplastics (Duromers)

2. How to control (fine tune) the properties

Strong and tough hydrogels crosslinked by multi-functional polymer colloids



JOURNAL OF POLYMER SCIENCE, PART B: POLYMER PHYSICS **2018**, 56, 1336–1350

3. Characterization methods

Primary structure: chemical structure, tacticity FTIR, NMR, Raman, x-ray powder diffraction (XRD)

Secondary and terciary structures: Conformation, configuration, subtle structural changes

Scattering methods: light scattering, Small-angle X-ray scattering (SAXS, crystalline structure), Small-angle Neutron Scattering (SANS), viscosity (scaling)

Circular Dichroism

Wide-angle X-ray scattering, WAXS (relationship between the structure and the mechanical properties)

Molar mass and mass distribution, polydispersity

Chromatography, light scattering, viscosity, sedimentation, interaction chromatography, fractionation (SEC-MALS), MALDI-TOF

Thermal properties

Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), glass transition temperature and melting point.

Thermogravimetry (stability and composition)

Diffusion properties

dynamic light scattering, field flow fractionation, 2D NMR

Branching

light scattering and viscometry (long chain branching), spectroscopy/end group number (short chain branching)

Rheology

mechanical stress-strain tests, melt viscosity, processing

Optical properties

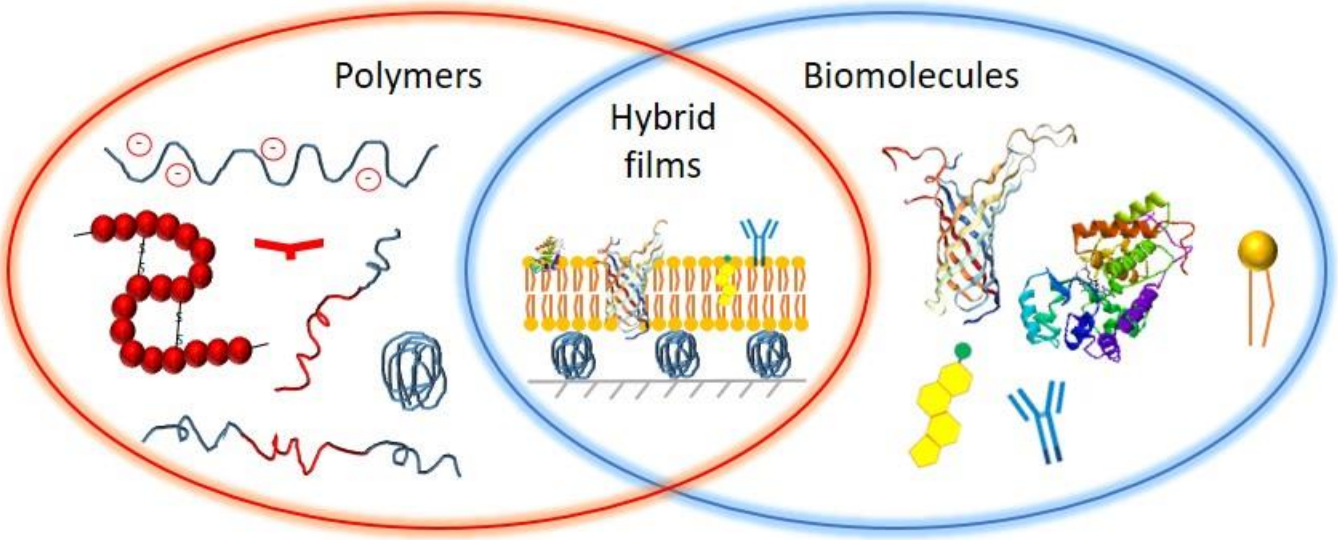
Transmittance at UV–vis–NIR, refractive index

4. Physico-chemical characterization of biohybrid polymer compartments

Reliable and reproducible methods should be used to characterize **their dimensions, shape, and morphology** as well as the **properties of the synthetic membranes such as polarity, surface charge, elasticity, thickness, permeability and lamellarity. Properties and functionality of the incorporated biomolecules** (e.g. enzyme activity, selectivity of pores, specificity of antibodies) must be shown.

Methods for **size and morphology** determination can be roughly divided into:

- **Techniques for direct visualization, mainly microscopy**
- **Techniques based on the scattering of radiation**



4. Physico-chemical characterization of biohybrid polymer compartments

Techniques for direct visualization

Nano-sized vesicles are investigated by:

- **Transmission electron microscopy (TEM)**
- **Cryo-techniques-** deformations are avoided- the samples preserve their original morphology. Membrane properties.
- **Atomic force microscopy (AFM)** belongs to the frequently applied techniques for size and topography of immobilized polymeric vesicles with the advantage that the measurements can be performed **in liquid- a biologically relevant environment while still having a nanometre resolution.** Mechanical properties like Young's modulus or bending modulus can be derived.

Larger vesicles in the micron range are investigated by:

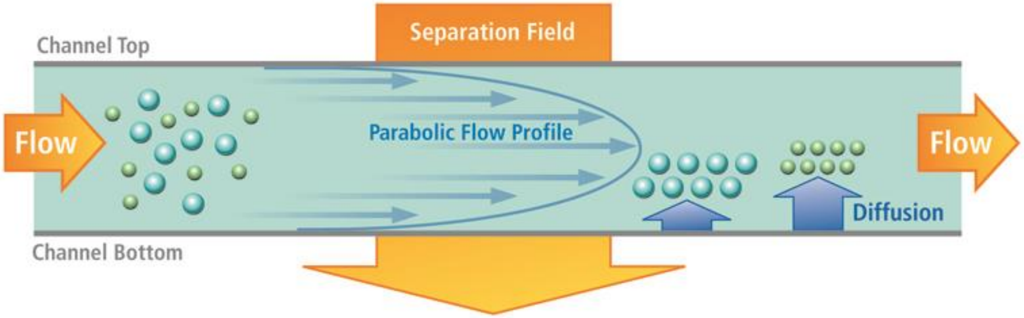
- **Light/fluorescence/confocal laser scanning microscopy.** Super-resolution techniques are used to overcome the diffraction limit of photons to expand fluorescence microscopy to nanoscale compartments: **SIM** (structured illumination microscopy), **SMLM** (single-molecule localization microscopy) combined with **sPAINT** (spectroscopic point accumulation for imaging in nanoscale topography) or **STORM** (stochastic optical reconstruction microscopy) combined with single molecule tracking.
- **Fluorescence correlation spectroscopy (FCS).** It analyses the fluctuations in fluorescence intensity of a small number of fluorescent particles/molecules within a very tiny volume due to diffusion (e.g. Brownian motion) by using temporal autocorrelation. Diffusion coefficients, hydrodynamic radii and concentrations can be derived from these data, which is especially useful to quantify and to investigate the behavior of fluorescently labelled biomolecules within the environment of the polymeric membranes or inside compartments

4. Physico-chemical characterization of biohybrid polymer compartments

Techniques based on the scattering of radiation

- **Laser light scattering,** measurements for simultaneous size and morphology determination of nanosized compartments.
- **Dynamic light scattering (DLS),** the intensity fluctuations of the scattered laser light due to the Brownian motion of the vesicles are used to determine the hydrodynamic radius by Stokes–Einstein relation.
- **Static light scattering (SLS),** information about the morphology by the radius of gyration.
- **Elastic scattering of neutrons (SANS) or X-rays (SAXS)** at small angles can be used to get more detailed information about the morphology, shape and structure of polymeric membranes and compartments, but is limited by the need of appropriate radiation facilities.

- Other techniques such as flow cytometry, size exclusion chromatography (SEC), asymmetrical flow field-flow fractionation (AF4))- Structural and mechanical properties of polymeric vesicles are also subject of computational studies using coarse-grained simulations such as dissipative particle dynamics. Shape transformation, rupture, fusion, and membrane characteristics could be simulated and used to explain experimental results.



4. Physico-chemical characterization of biohybrid polymer compartments

Direct Visualization of Vesicle Disassembly and Reassembly Using Photocleavable Dendrimers Elucidates Cargo Release Mechanisms

Shangda Li, Boao Xia, Bilal Javed, William D. Hasley, Adriel Melendez-Davila, Matthew Liu, Meir Kerzner, Shriya Agarwal, Qi Xiao, Paola Torre, Jessica G. Bermudez, Khosrow Rahimi, Nina Yu. Kostina, Martin Möller, Cesar Rodriguez-Emmenegger, Michael L. Klein, Virgil Percec*, and Matthew C. Good*

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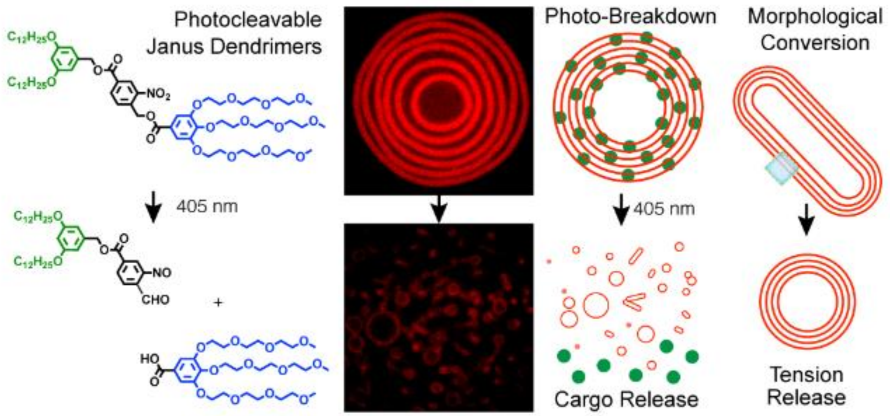

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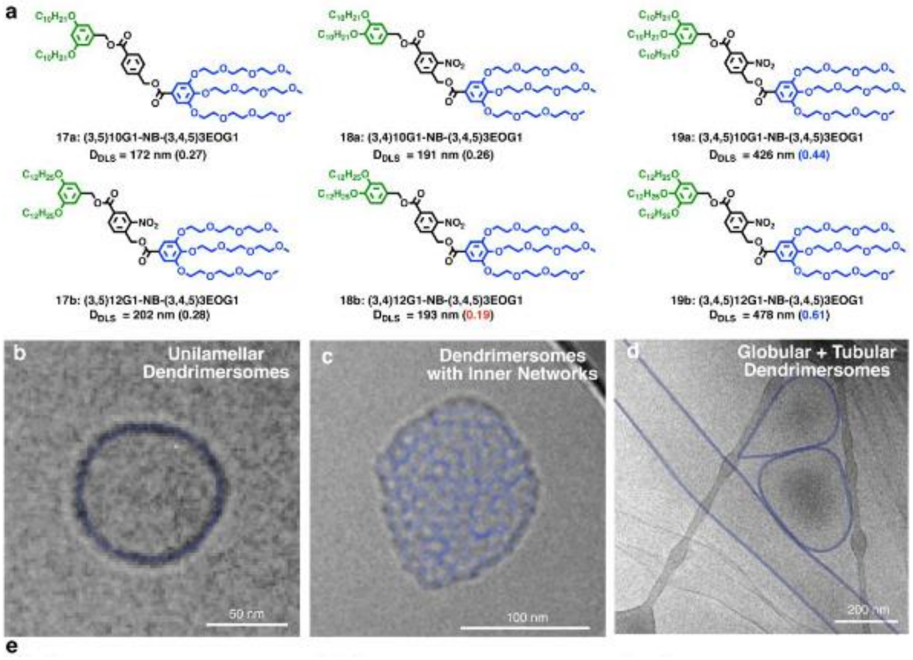
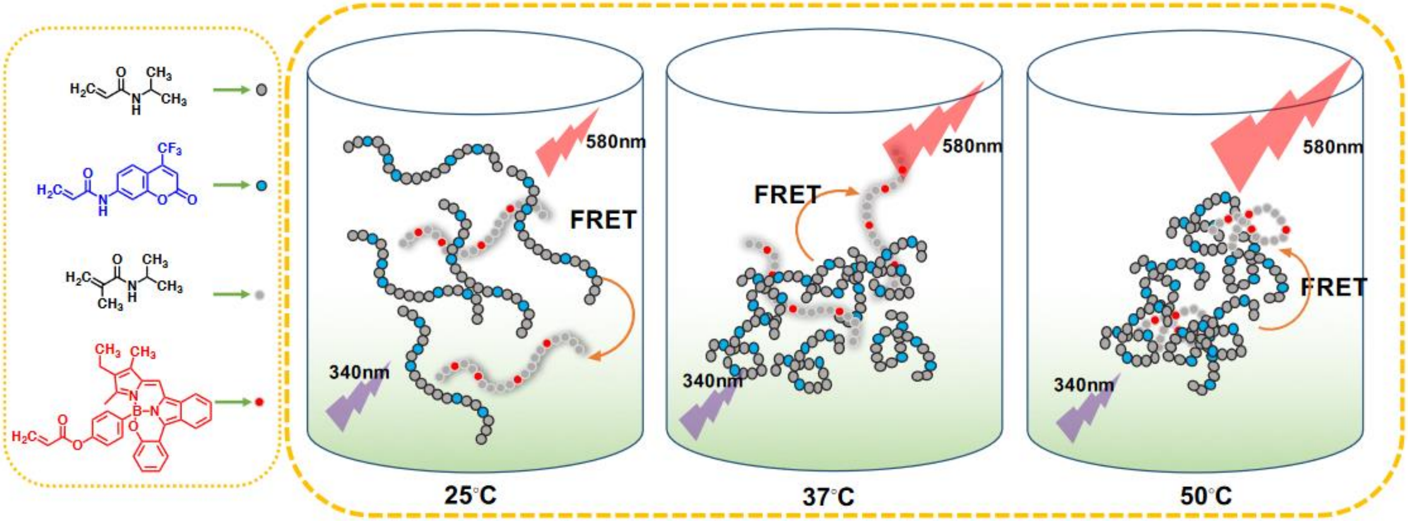
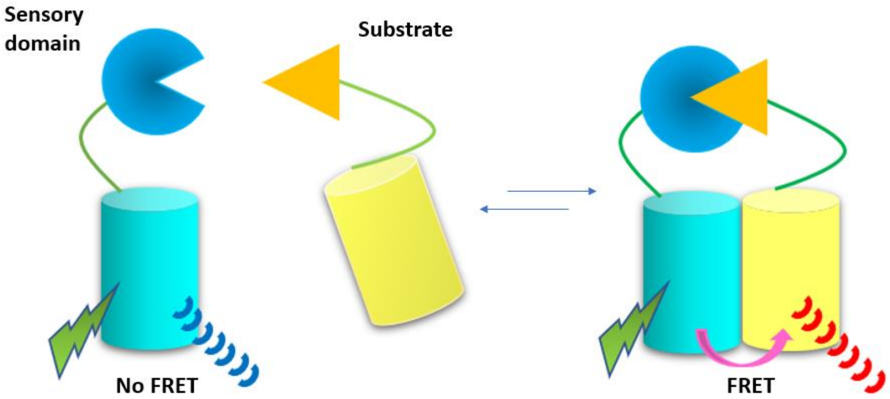


4. Physico-chemical characterization of biohybrid polymer compartments

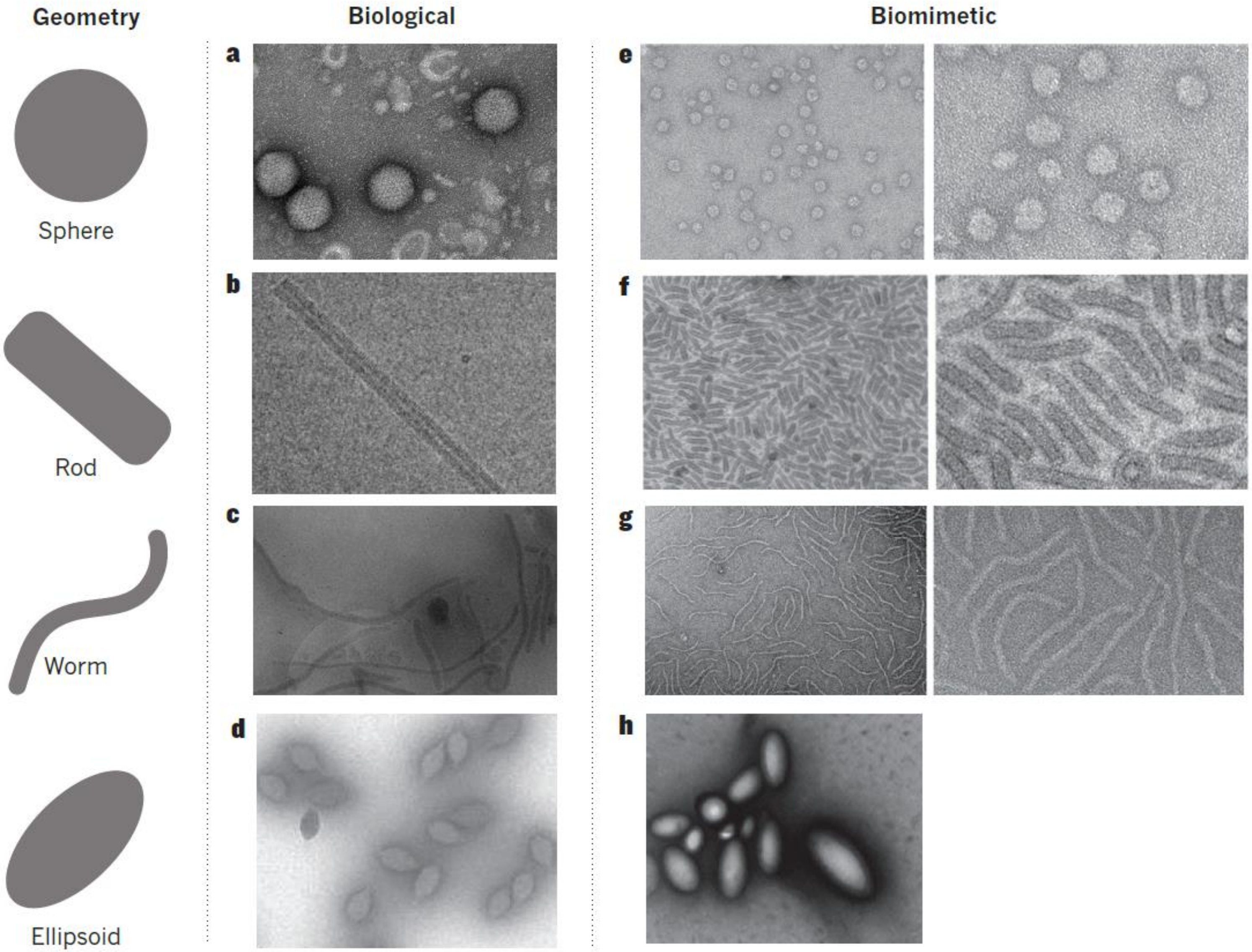
Thermo-Responsive Fluorescent Polymers with Diverse LCSTs for Ratiometric Temperature Sensing through FRET





Polymers2018,10, 283; doi:10.3390/polym10030283

5. Mimicking biological functionality with polymers for biomedical applications



*Jordan J. Green & Jennifer H. Elisseeff, Nature, 540, 386–394(**2016**)*

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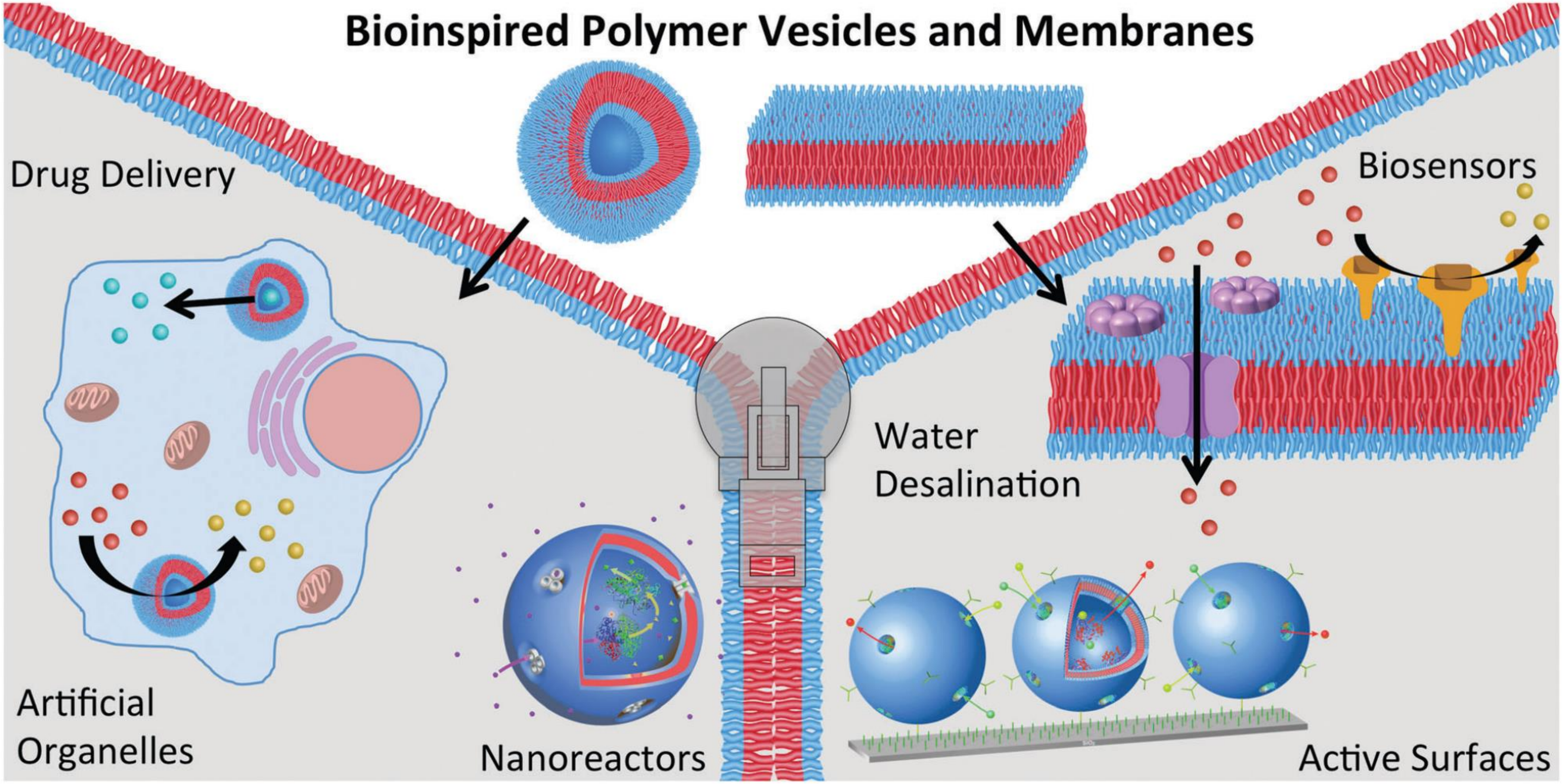
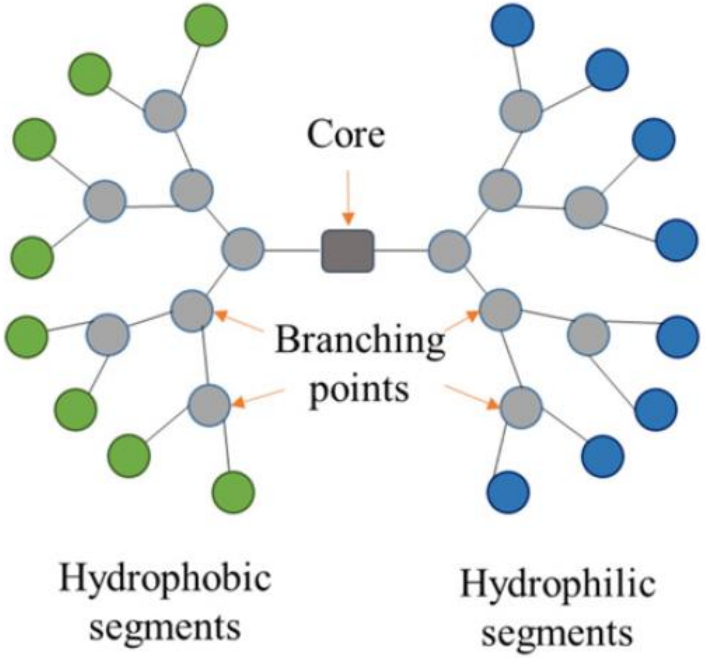
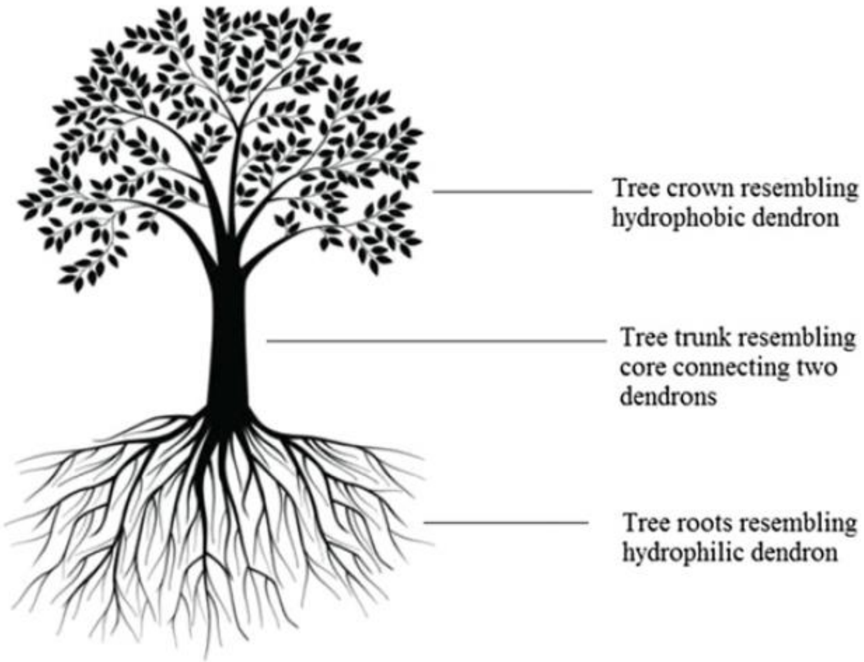


Cornelia G. Palivan, Chem. Soc. Rev., ***2016****,45, 377-411*

5. Mimicking biological functionality with polymers for biomedical applications





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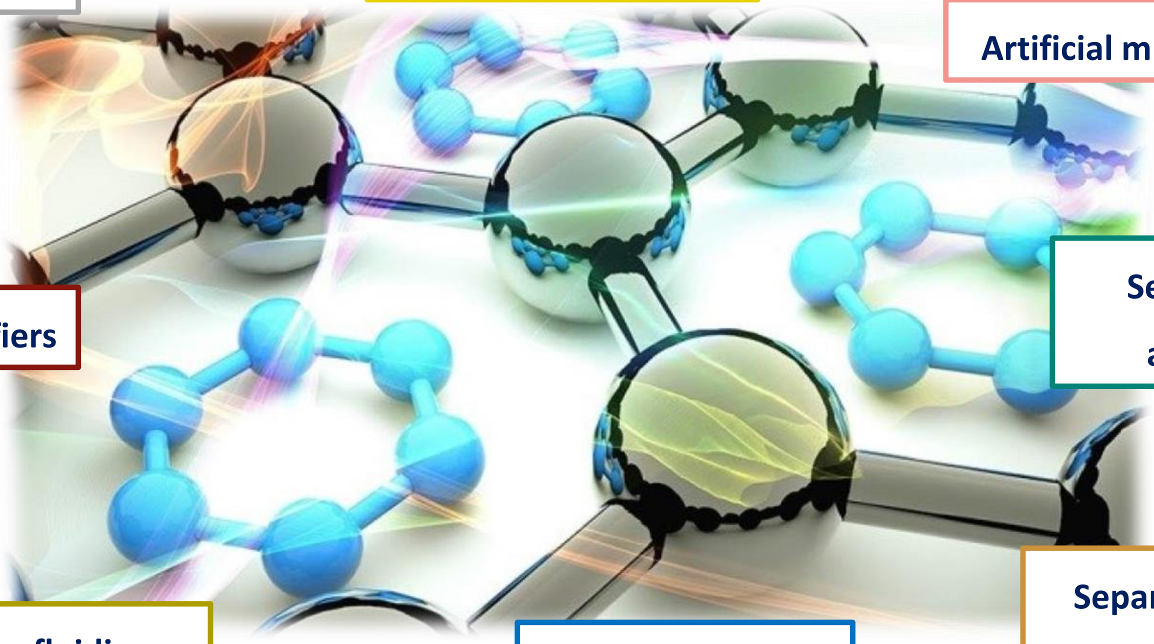
5. Smart Polymers. Applications

How smart are the polymers?



- Control release
- Self-healing materials
- Artificial muscles
- Viscosity modifiers
- Sensors and actuators
- Microfluidics devices
- Shape changing fibers
- Separation and purification

6. Example Questions

1. **Mention some methods for size and morphology determination of biohybrid polymers compartments**
2. **How we can tune the polymer properties**
3. **Two polymers with the same dispersity but with symmetric and asymmetric MWDs (shape) have the same properties**