Matter Structure: Gases, Liquids, Condensed (Crystal and Amorphous)

Alexei R. Khokhlov

Moscow State University

Lomonosov Moscow State University

Nowadays Moscow State University is a major traditional educational institution in Russia, it offers training in almost all branches of modern science and humanities.

Its undergraduates may choose one of 57 qualifications, while doctoral students may specialize in 168 different areas.

The total number of MSU students exceeds 40,000.

MSU is a Rapidly Growing University

In 2005 the new Fundamental Library of MSU was opened. Since then 6 more buildings were constructed, including a Medical Center.

This became possible because of significant help from the Moscow City Government

MSU is the Leading University in Russia

As a result of independent studies MSU holds the first place in:

1. The number of citations (each year more than 300,000 citations on the publications of scientists from MSU)
2. The quality of education (more than 60% of lecture courses given in the world are delivered in MSU)
3. The successful career of the graduates

In 2009 MSU obtained a special status by law (subordination directly to the Governement, not through the Ministry, special line in State Budget)

Priority areas for Moscow State University

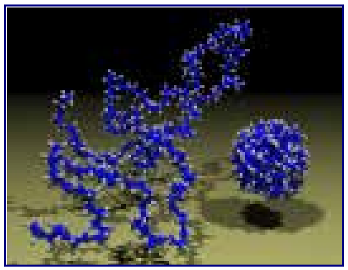
- Education
- Supercomputers
- Scientific Satellites
- Medicine
- Nanotechnologies for Energy/ Nanobiotechnologies
- Nature

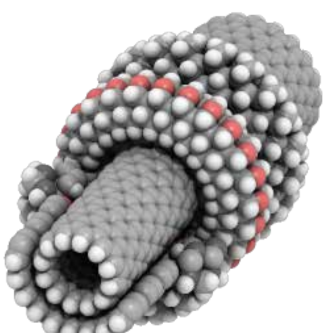
Educational and Research Center in Nanotechnologies

Aim:

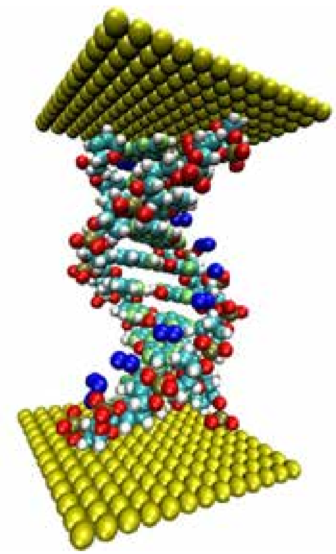
- development new multidisciplinary educational programs in field of modern nanotechnologies

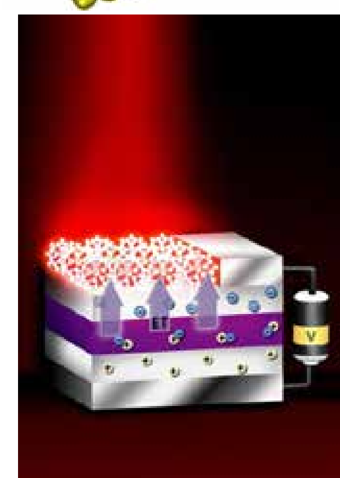
Three Specialization in Nanotechnologies

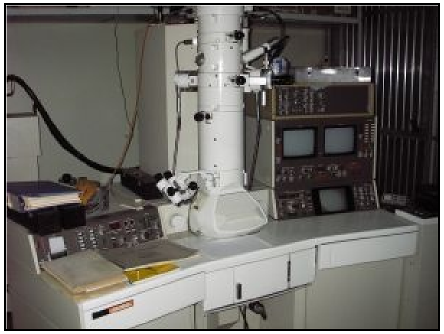




- Nanosystems and nanodevices;
- Functional nanomaterial
- Nanobiomaterials and nanobiotechnologies







Important aspect of education in nanotechnologies modern well – equipped practicum.

Supercomputer Center of MSU

Computer facility at past

1956 г.

Computer "Strela" - the first
Soviet serial computer
Retained about 2,000 operation/s

Computer facility nowadays

2011 г.

2009 Supercomputer “Lomonosov”
415 T flops (12th place in the world and second place in Europe), in March 2011 it was upgraded to 1300 T flops using GPU architecture

Info from the secondary school program: three states of matter: gases, liquids and solids (understood as crystalline solids).

Normally soft matter (amorphous solids) is not mentioned. Meanwhile, we are surrounded mainly by the soft matter and we are ourselves soft matter.

Soft matter research require special language (e.g. scaling arguments). And the role of computer simulations is more central than for other states of matter.

Polymers constitute a central topic of soft matter agenda.

What is a polymer?

Polymers are long linear chains consisting of a large (*N* >>1) number of monomer units.

For synthetic polymers usually $N \sim 10^2 - 10^4$;

For DNA $N \sim 10^9 - 10^{10}$.

$$-CH_2-CH_2-CH_2-CH_2-$$

polyethylene

polystyrene

polyvinylchloride

Polymers as long molecular chains

Electronic microphotograph of DNA macromolecule, partially released through the defects of a membrane

Polymers around us

Plastics

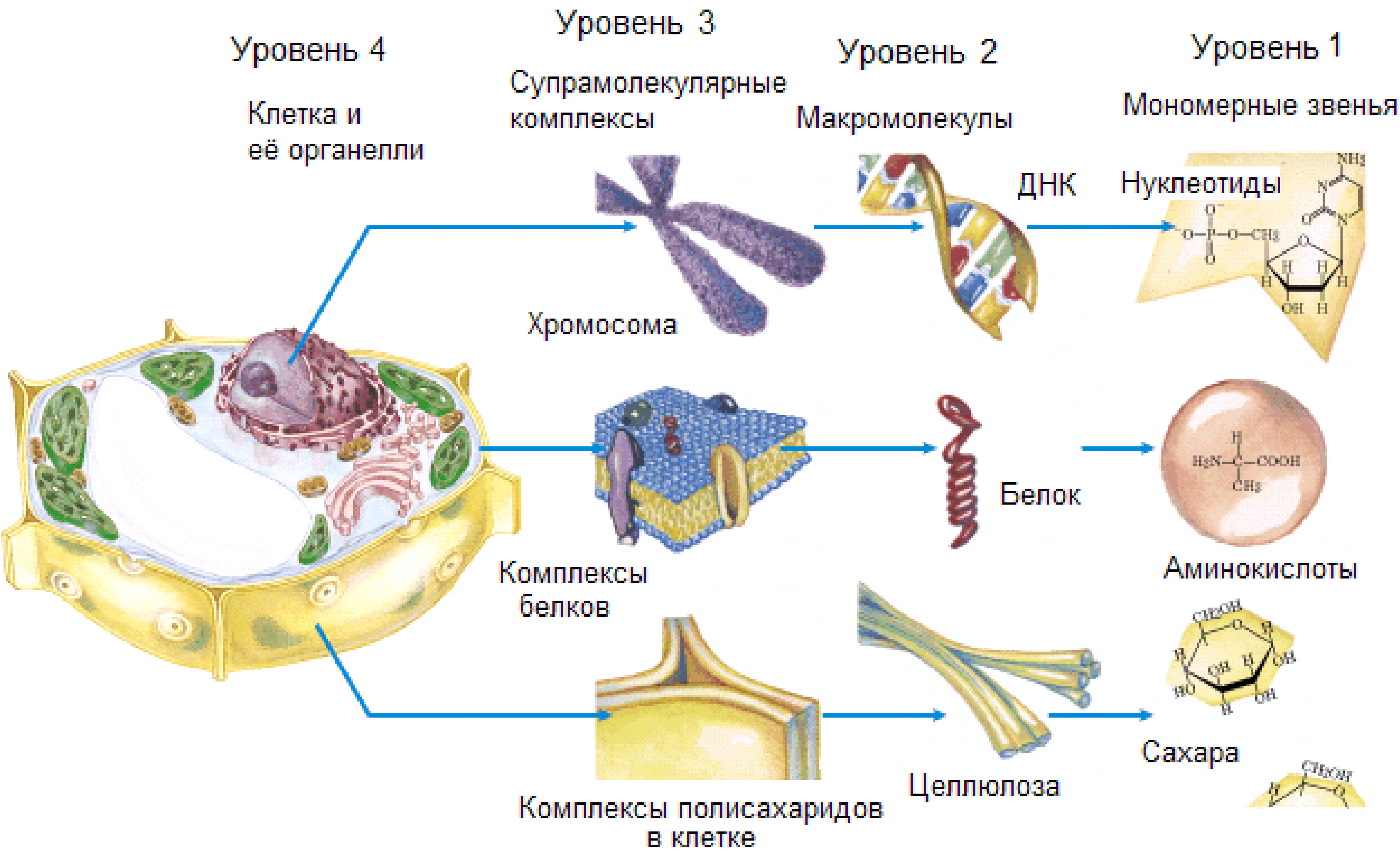
Resins

Fibers

Films

Polymers around us

Living Systems



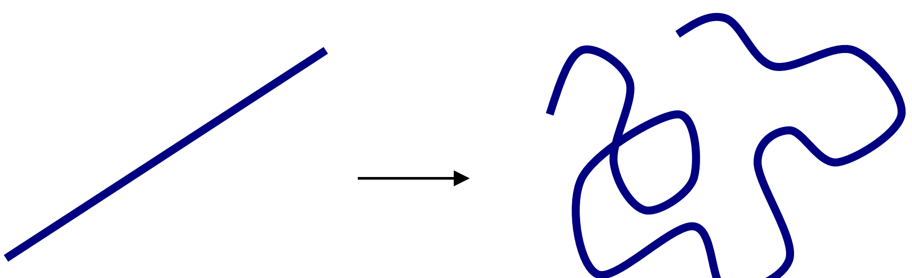
Physical properties of polymers are based on three main factors:

1. Monomer units are connected into long chains.
   They do not have the freedom of independent translational motion.

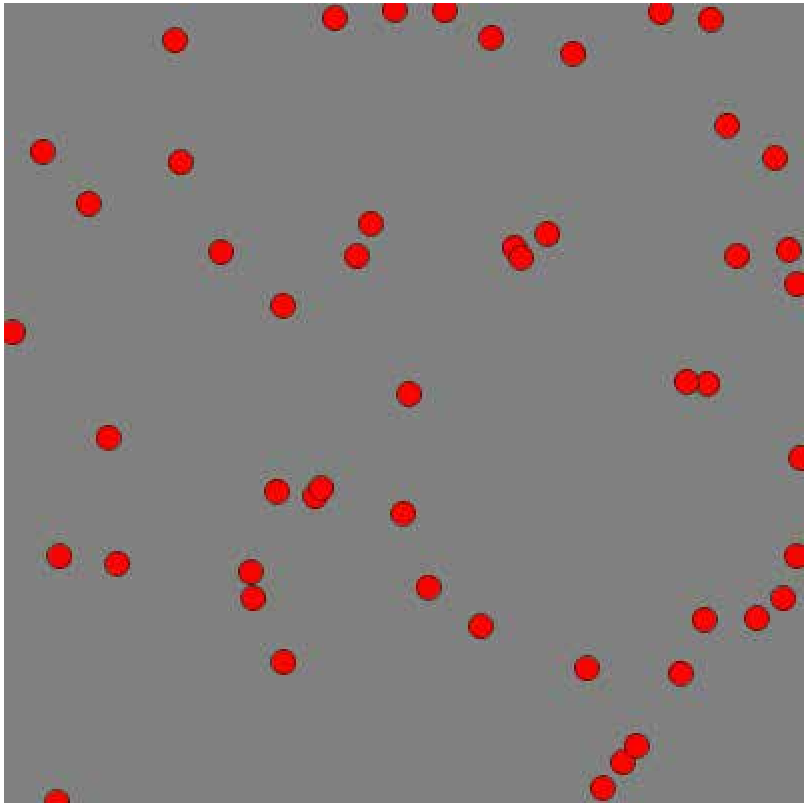
   Polymer systems are poor in entropy.

2. Number of monomer units is large $N >> 1$.

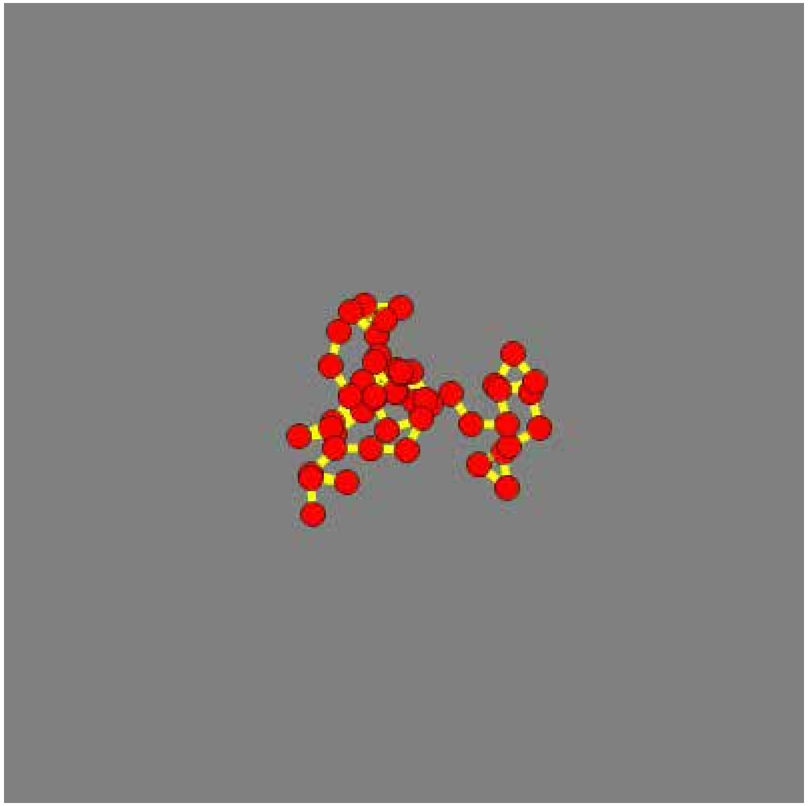
3. Polymer chains are flexible.



It is the low entropy that makes polymers capable to self-organisation: even small energetic interactions lead to the ordering in the position of atomic groups



Ideal gas



Freely-jointed polymer chain

Some Facts from the History of Polymer Science

Polymer Science started approx. from **1930** after **H.Staudinger** proved that **polymers** are **long molecular chains**.

In **1930-1933** classical theory of high elasticity of rubbers was developed based solely on the fact that **elastomers** are **polymer networks consisting of long flexible molecular chains** (**W.Kuhn, E.Guth, H.Mark**).

During the **first years** of polymer science **mechanical properties** of polymers received **most of attention**, i.e. **polymers** were considered mainly as **construction materials** (**plastics, rubbers, fibers** etc.).

Some Facts from the History of Polymer Science

After **Watson** and **Krick** discovered in **1953** the **DNA double helix**, it became clear that **biopolymer macromolecules** implement **most important functions in living systems**. Hence the attention to functional polymers in general (**conducting polymers, optical polymers, superabsorbers, drug delivery systems** etc.). Approx. starting from **1980** research on **functional polymers** became **a mainstream in polymer science**.

Starting from approx. **2000** we are discussing also **smart polymers**. **Smart polymers = functional polymers** with **complex functions** (often depending on the external conditions).

Some Facts from the History of Polymer Education

Before **mid-fifties** it was **no special educational programs** in polymer science. **Polymers** were considered **as a part of colloidal science**.

In **mid-fifties V.A.Kargin** at **Lomonosov Moscow State University** and **H.Mark** at **Brooklyn Polytechnic** founded two **first educational departments in polymer science**.

After that specialized departments dedicated solely to polymer science appeared in many world universities. This process was **significantly accelerated** because of charismatic personalities of **P.J.Flor**y and **P.G.de Gennes** who contributed a lot to advertising of the **importance of polymer science**.

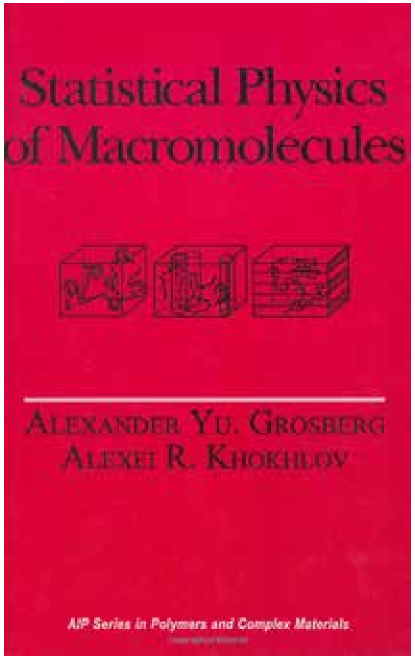
Starting from approx. **1975** **many world universities taught** their students how to **"think poly".**

My Modest Contribution

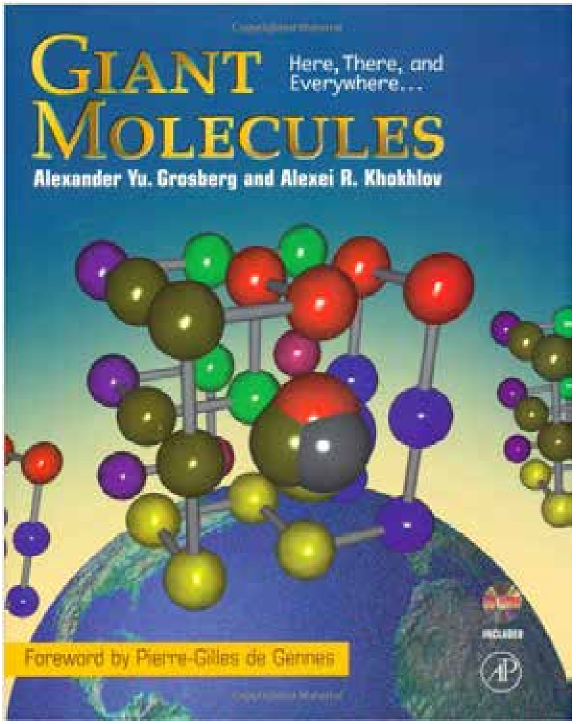
Starting from **1985** I organized the **education in polymer science** at the **Physics Department of Lomonosov Moscow State University** (special Department in Polymer Physics from 1993). About **70 scientists** obtained **PhD** in polymer physics from this **Department**. We tried to teach those people how to **"think poly"**.

Books for polymer education (written together with Prof.A.Yu.Grosberg):

Statistical Physics of Macromolecules (American Institute of Physics, 1994)



Giant Molecules: Here, There and Everywhere (Academic Press, 1997)



Nanotechnology boom in Russia 2005-2008

- Nanotechnology was officially considered as a mainstream in modern natural sciences
- Federal program "Infrasrtructure of Nanotechnologies in Russia" was adopted
- Kurchatov Institute was appointed as a coordinator of nanotechnology activities in Russia
- State Corporation for Nanotechnologies "Rusnano" was organised for commercialization of nanotech projects

Joining the "Nano" Trend

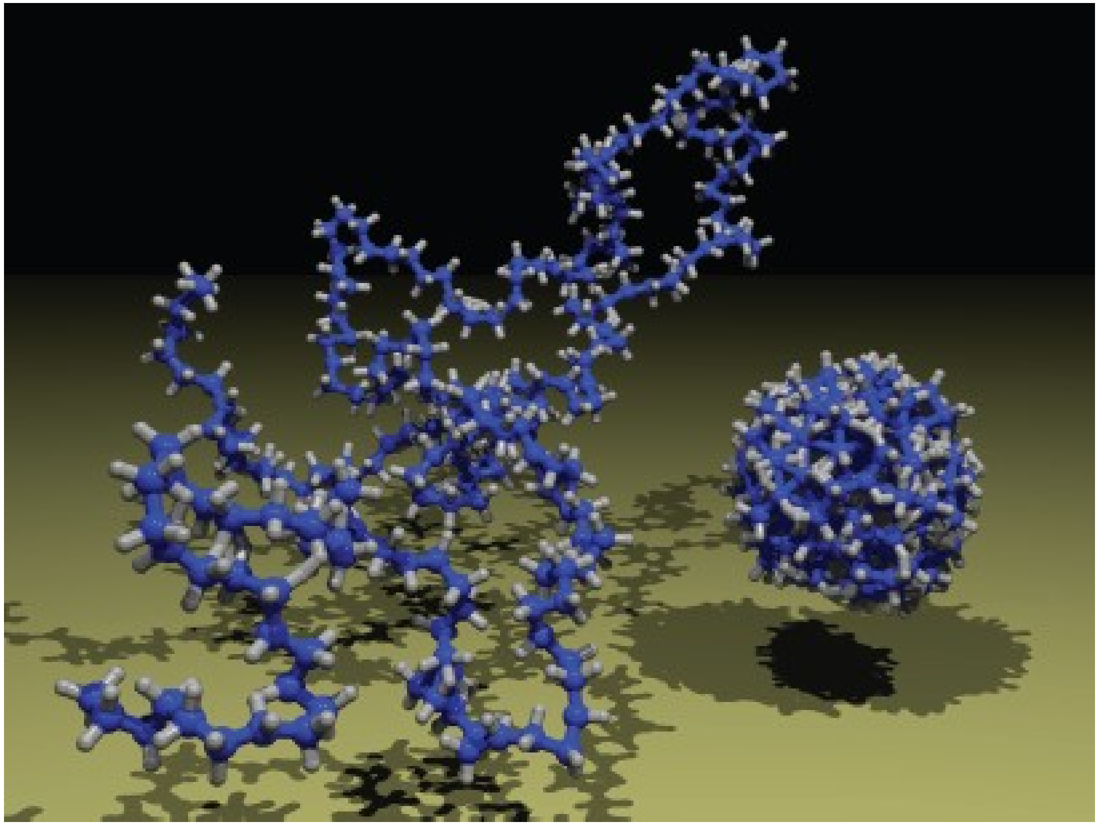
Polymers are obviously **"nano"**: typical characteristic size of **polymer coil** is **50 nm**, of **polymer globule 5 nm**, of **microstructures in block copolymers 10 nm**.

But what is also valuable is **multidisciplinarity idea** inherent in **"think nano"**. For polymers this was always the case (physics, chemistry, biology, mechanics, materials science are equally important).

Another favorable aspect is an enhanced vector towards **the applications** (this is familiar for polymers as well).

Conclusion: **polymers** is a natural part of **"nano" curriculum**.

For polymers nano-scale is emerging naturally

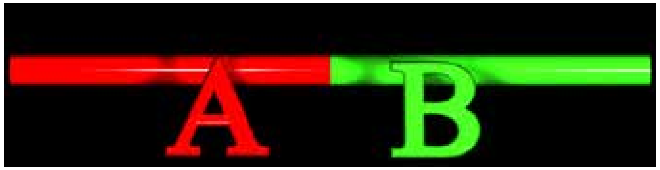


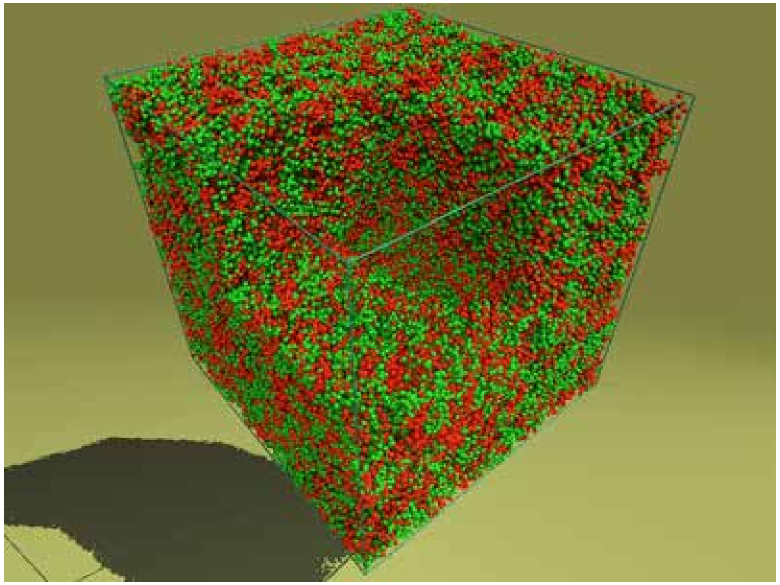
Polymer coil (ca 50 nm) and polymer globule (ca 5 nm)

Self-organization of polymer nanostructures

Microphase separation:
(scale ~10-100 nm)

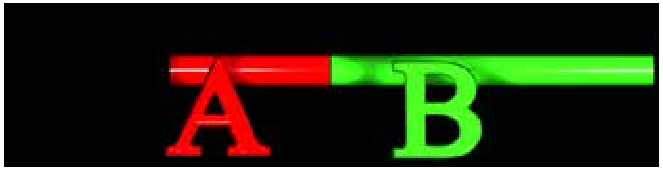
LAM

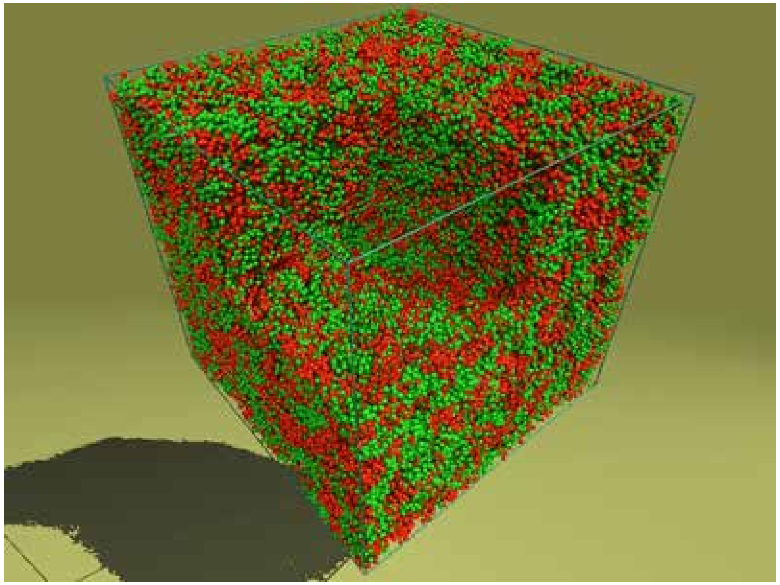




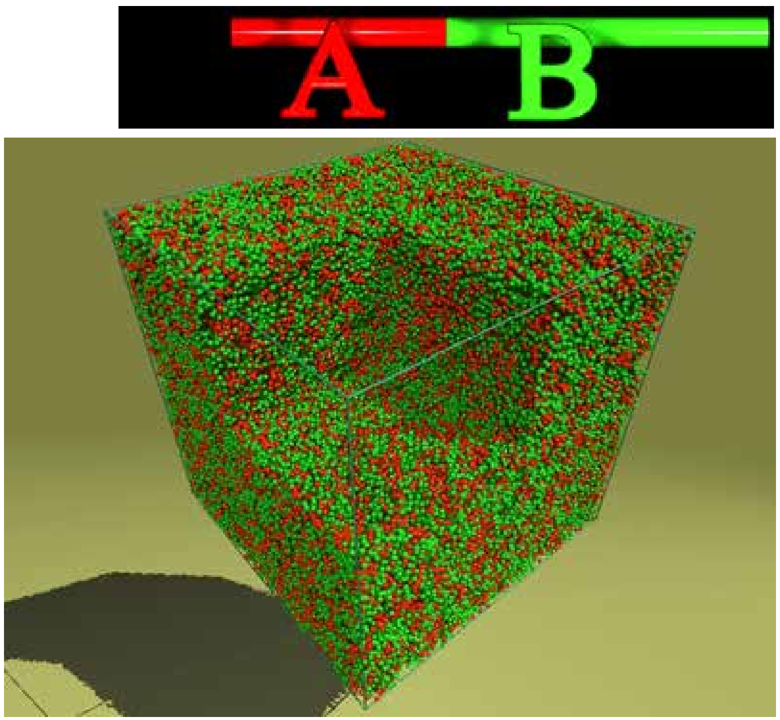
100 nm

HEX



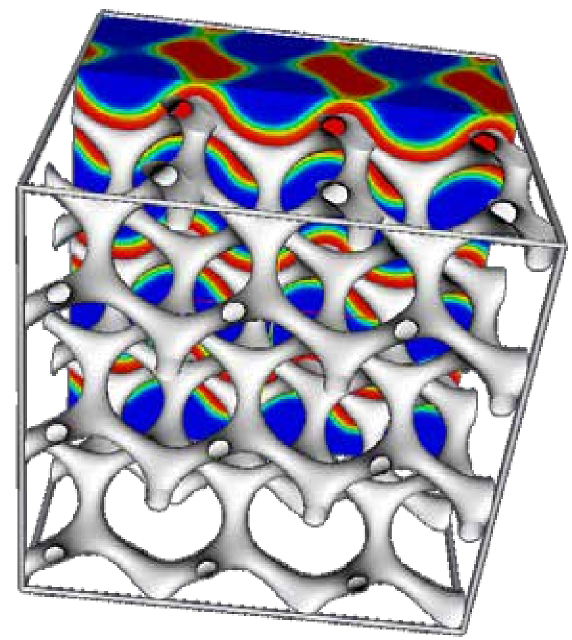


Self-organization of polymer nanostructures



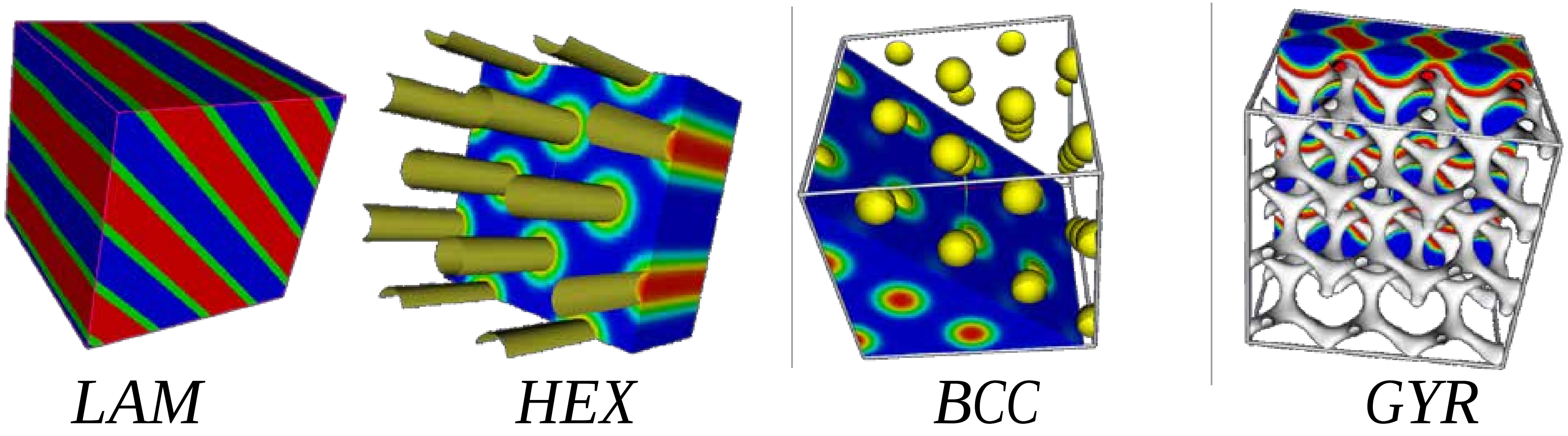
Particles

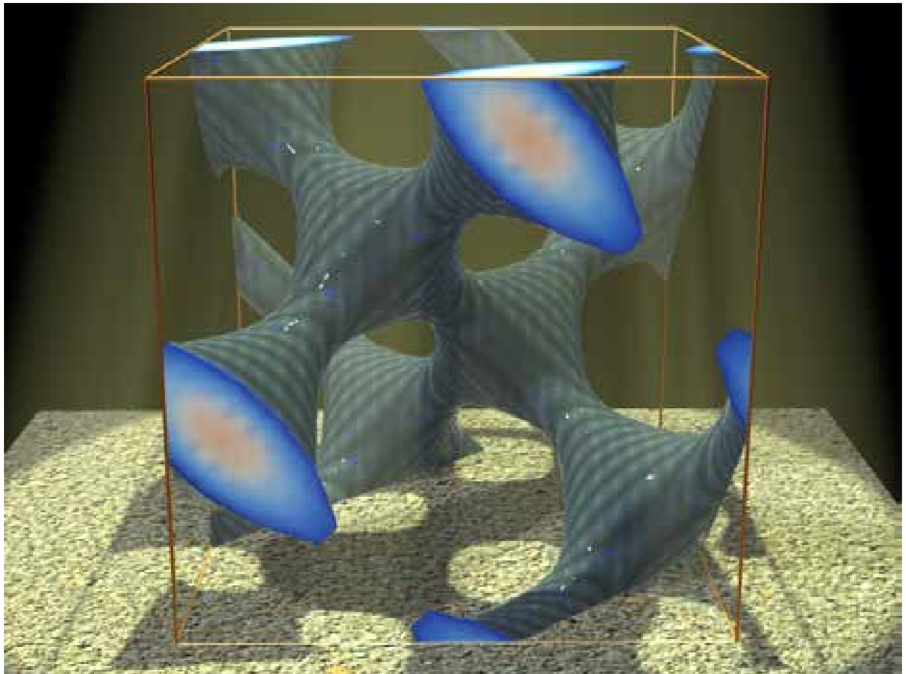
GYR

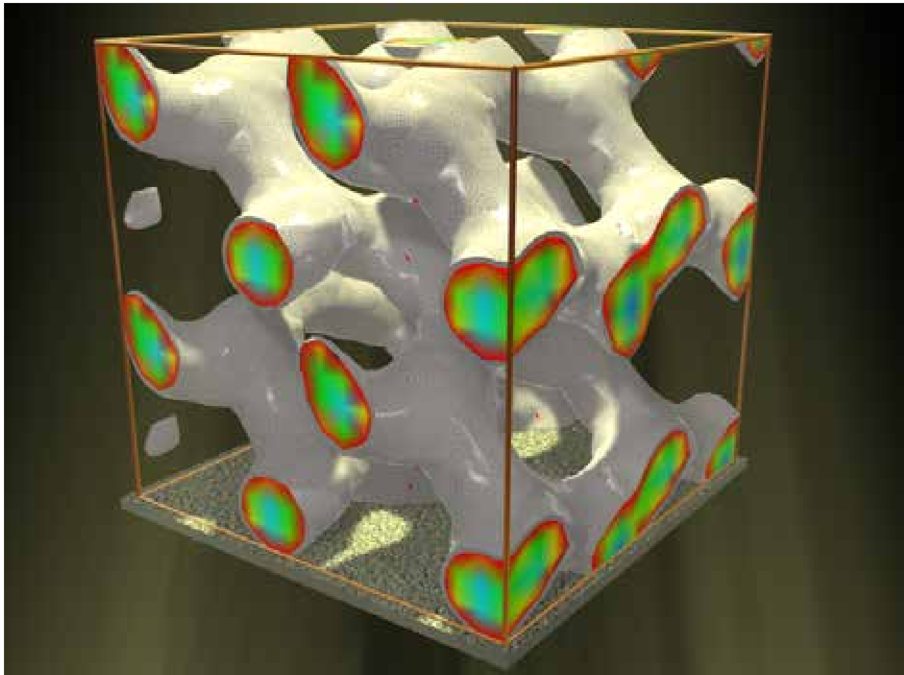


Field representation

Design of Polymer Nanostructures







Joining the "Nano" Trend

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But what is also valuable is **multidisciplinarity idea** inherent in **"think nano"**. For polymers this was always the case (physics, chemistry, biology, mechanics, materials science are equally important).

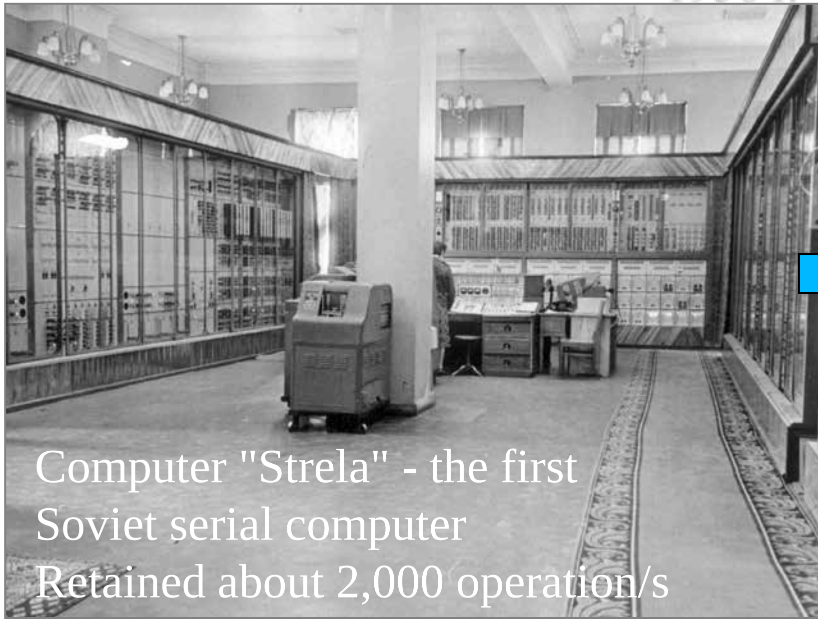
Another favorable aspect is an enhanced vector towards **the applications** (this is familiar for polymers as well).

Conclusion: **polymers** is a natural part of **"soft nano" curriculum**.

Supercomputer Center of MSU

Computer facility at past

1956 г.

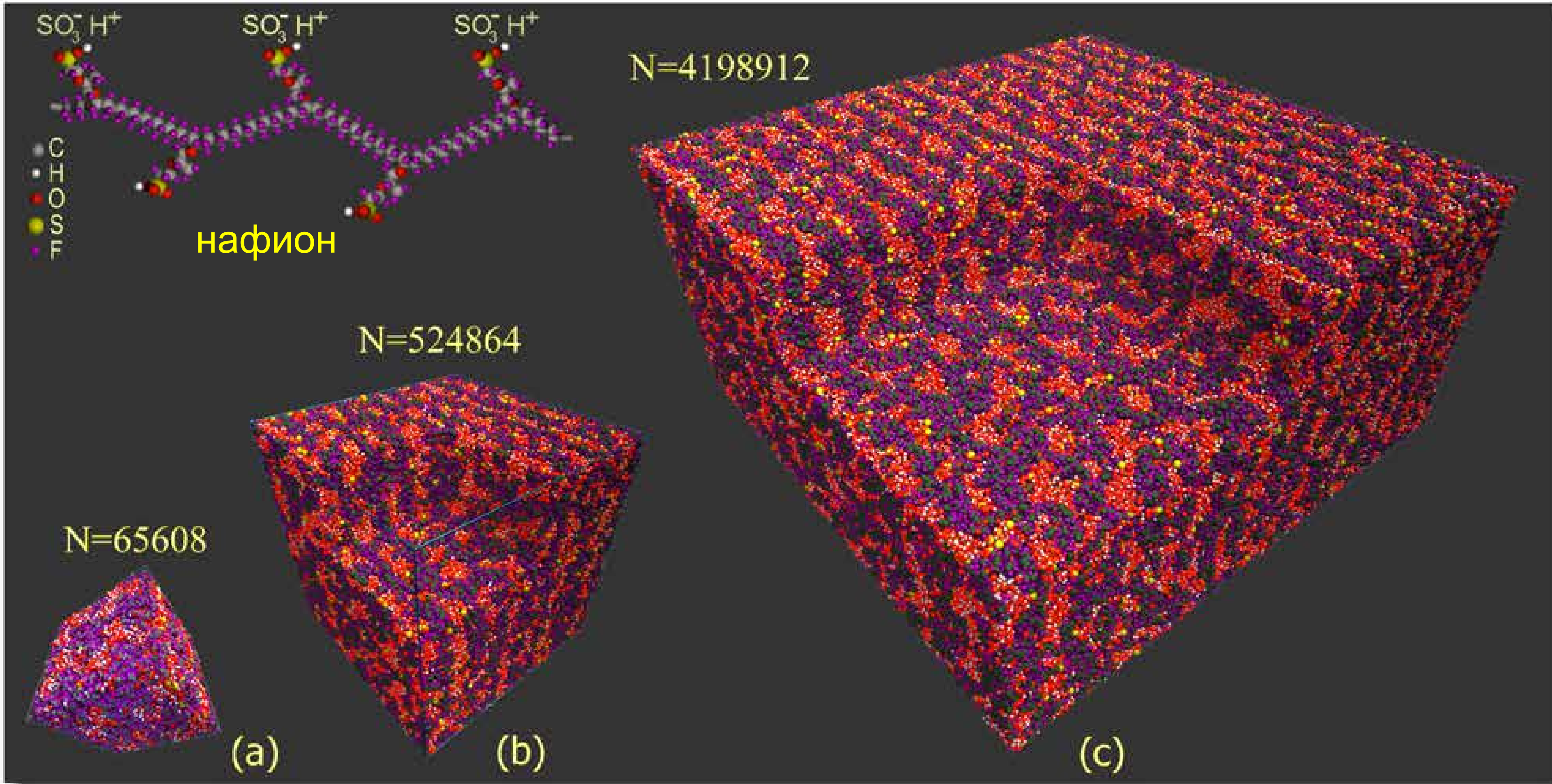


Computer facility nowadays

2011 г.

2009 Supercomputer "Lomonosov"
415 T flops (12th place in the world and second place in Europe), in March 2011 it was upgraded to 1300 T flops using GPU architecture

Nafion membrane: classical molecular dynamics
(record large-scale modeling using LAMMPS program)

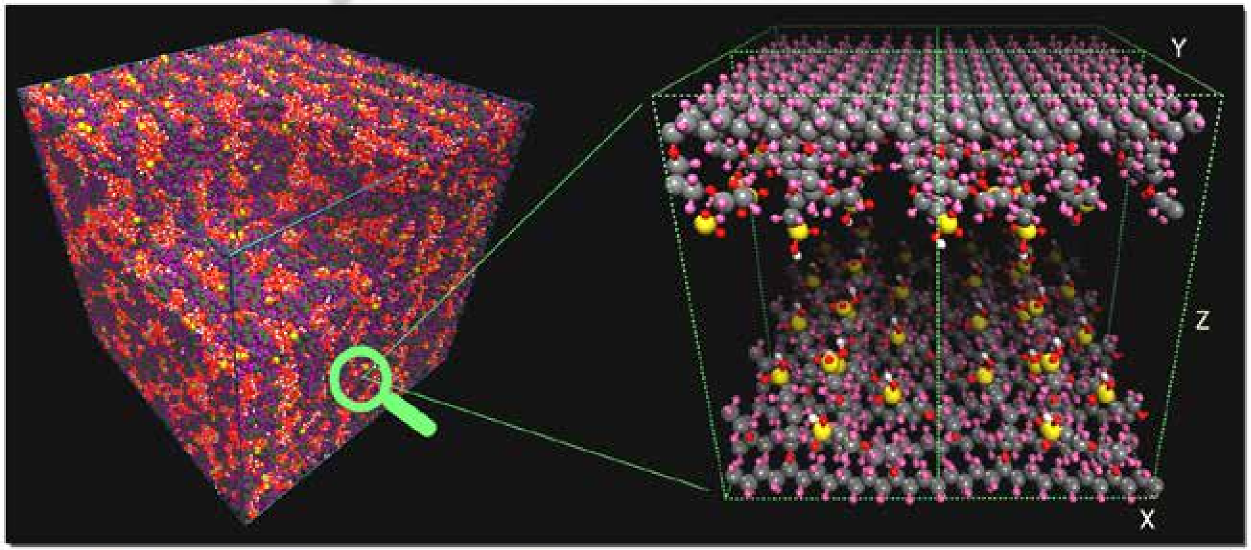


Even small water content leads to the proton conductivity

Nafion Membrane: Quantum molecular dynamics
(record modeling of ion-conducting channel with the package CP2k)

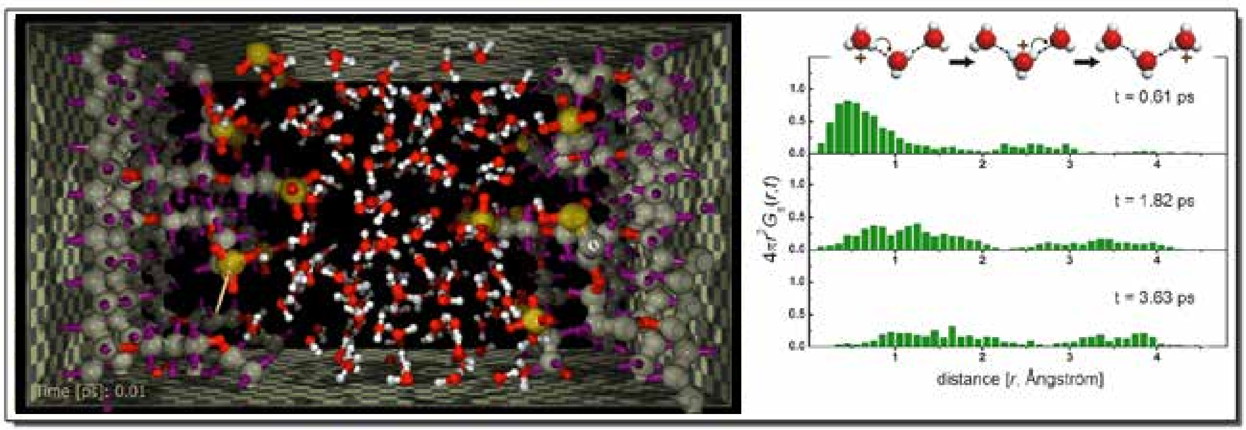
Charge transfer and Grotthus mechanism

Atomistic structure

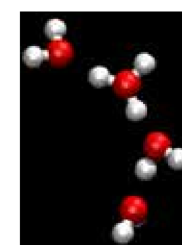


Model of channel

Quantum mol.dynamics (1200 atoms)



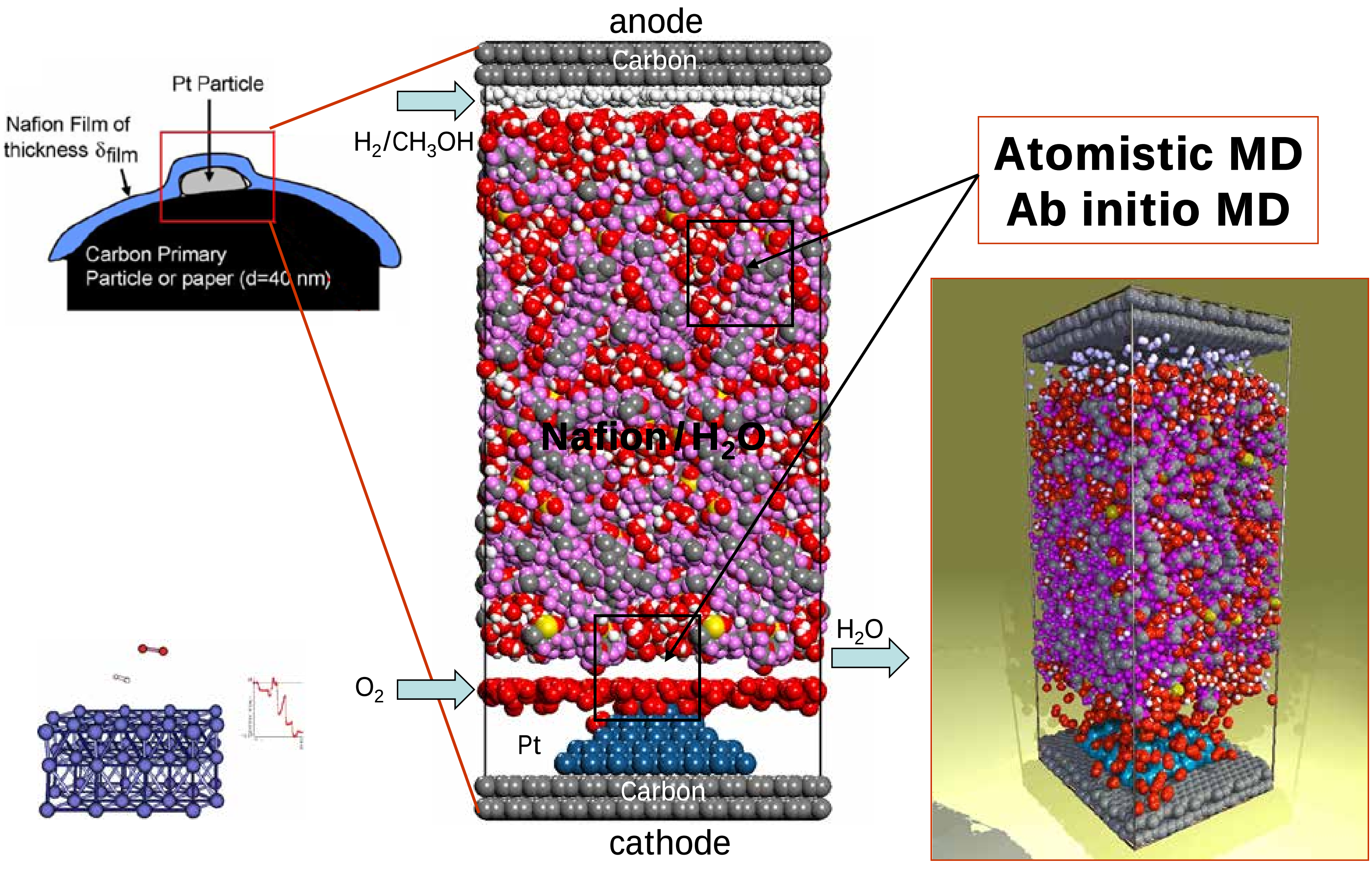
Charge transfer



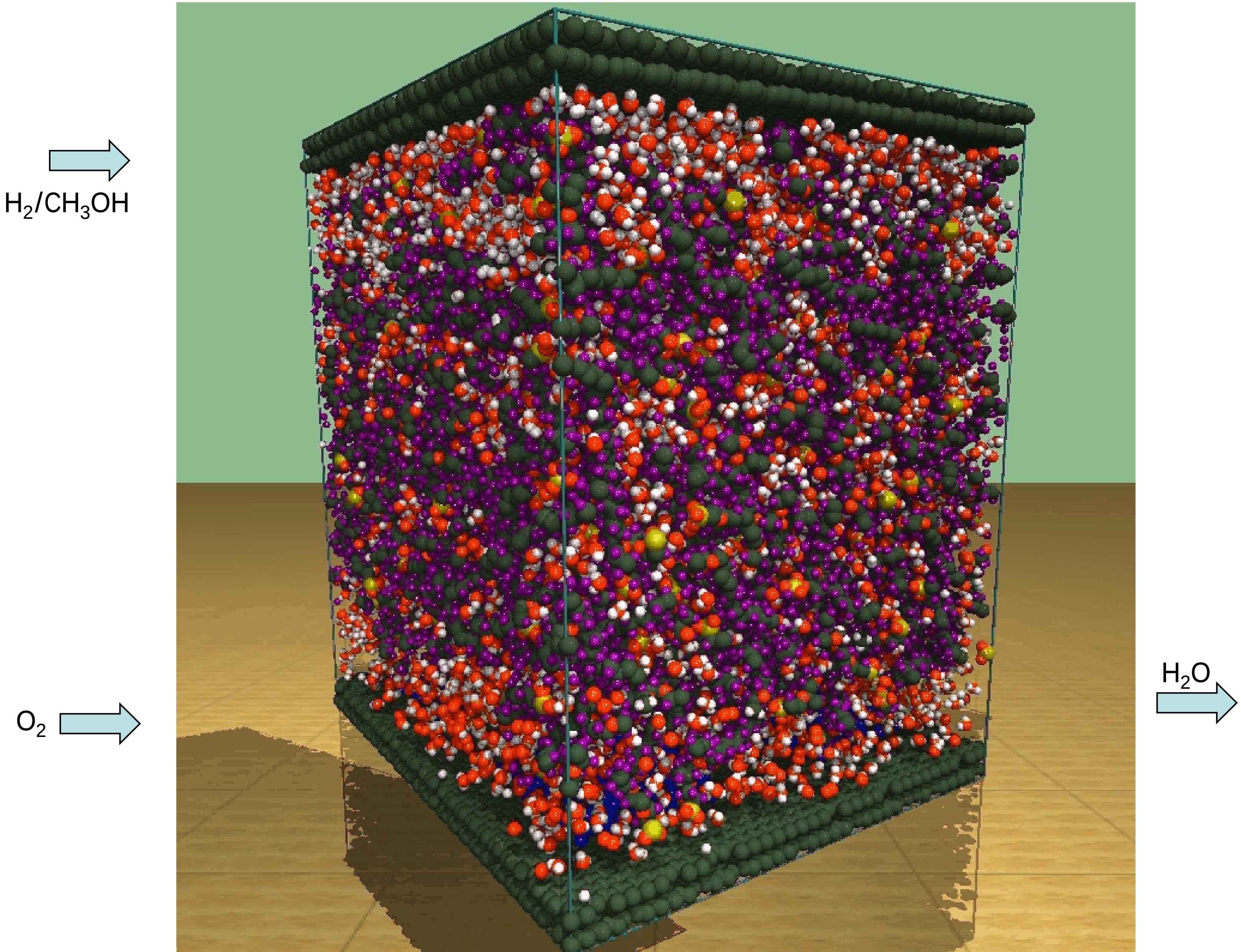
We used a hybrid approach within the framewok of the density functional theory (DFT) combining Born-Oppenheimer quantum molecular dynamics (BOMD) and Carr-Parinello method(CPMD)

The observed bimodality of Van Hove spatio-temporal correlation function $G_s(r,t)$ gives a first direct evidence of Grotthus mechanism

Atomistic model of the overall PEM FC,
including cathode, anode, and interfaces.

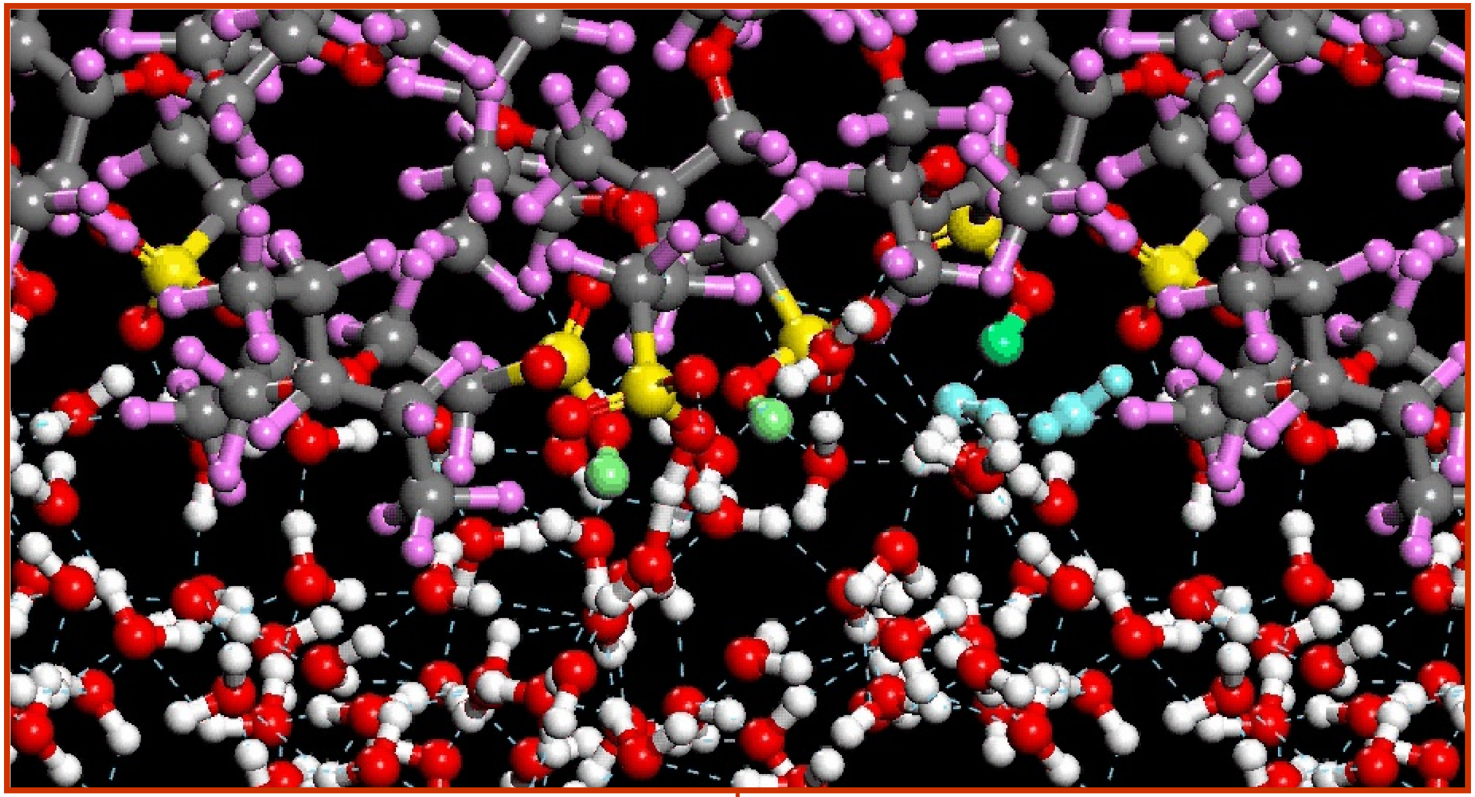


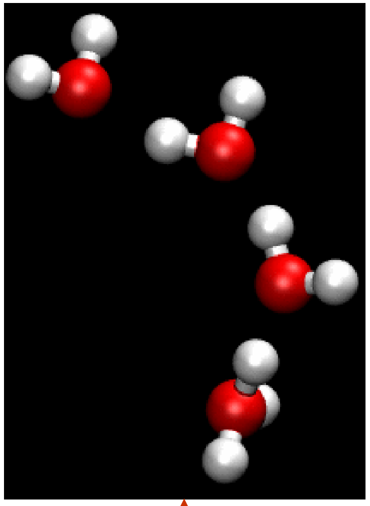
Fully atomistic molecular dynamics



First principles (*ab initio*) molecular dynamics: Hydrated Nafion membrane

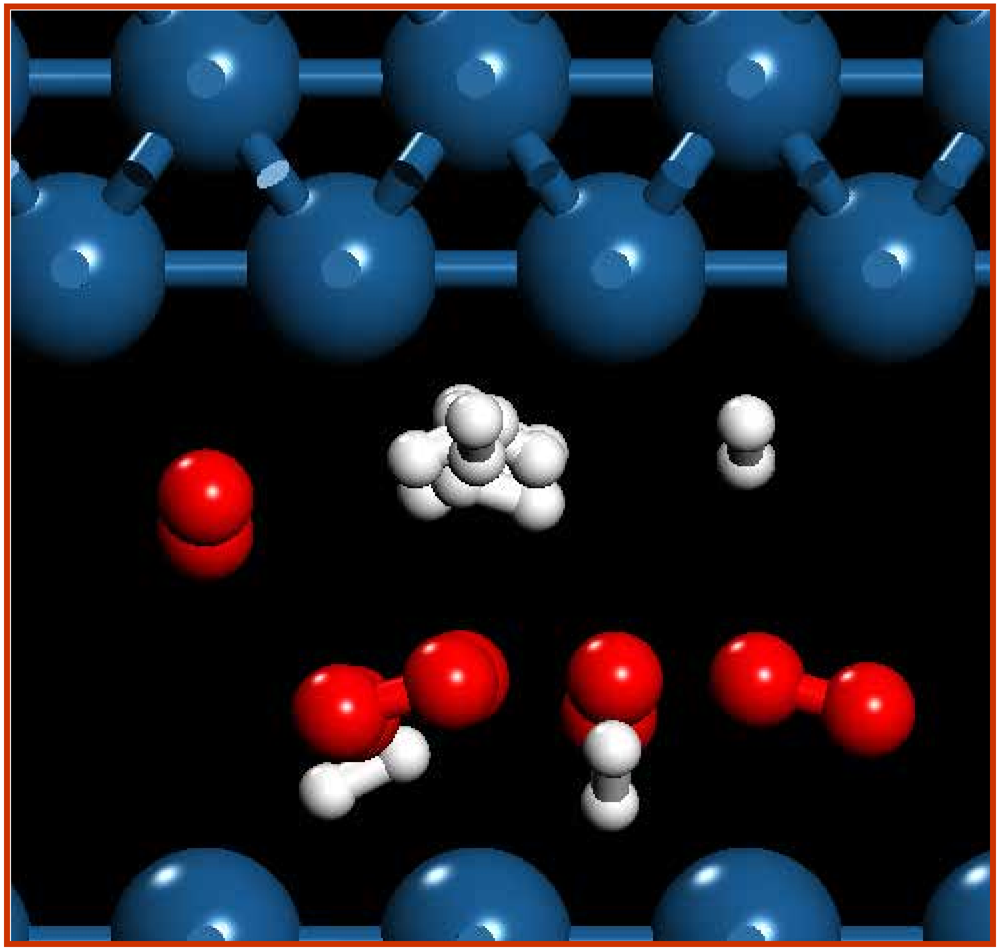
Large-scale simulations on petaflop-level supercomputers

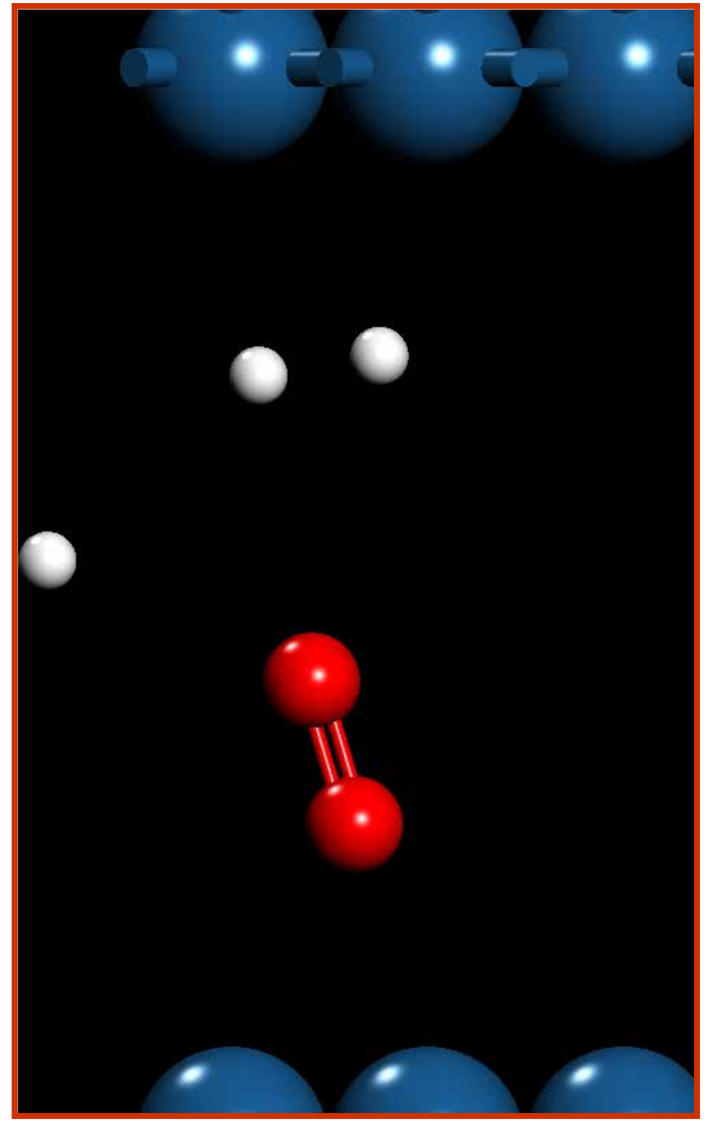




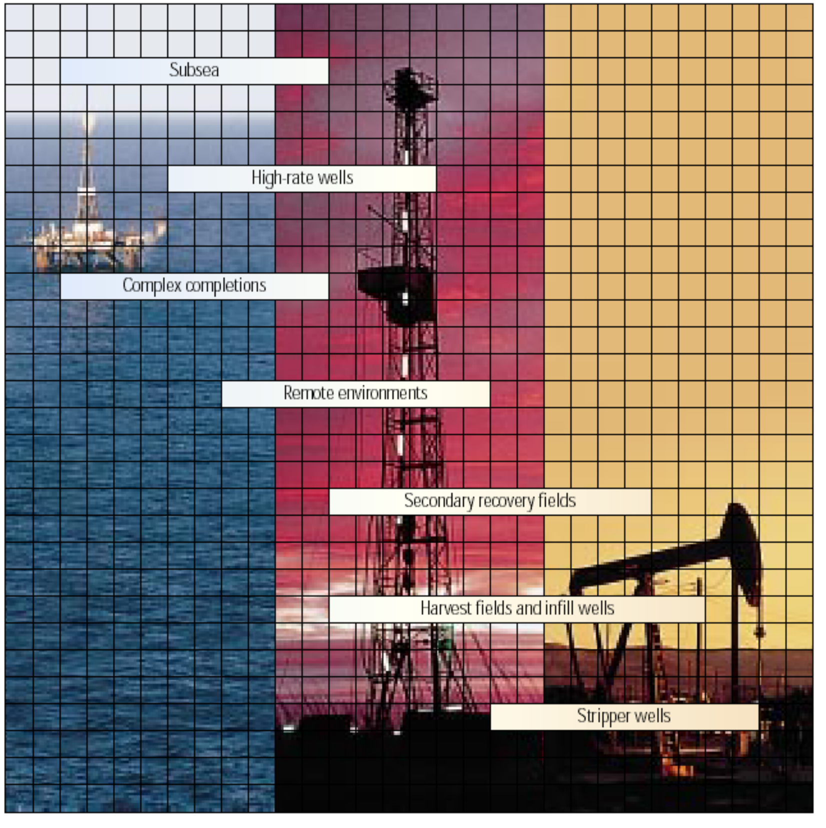
The Grotthuss mechanism by which an 'excess' proton from SO_3H diffuses through the hydrogen bond network of water molecules through the formation/cleavage of covalent bonds.

First principles (*ab initio*) molecular dynamics: Formation of water on platinum surface





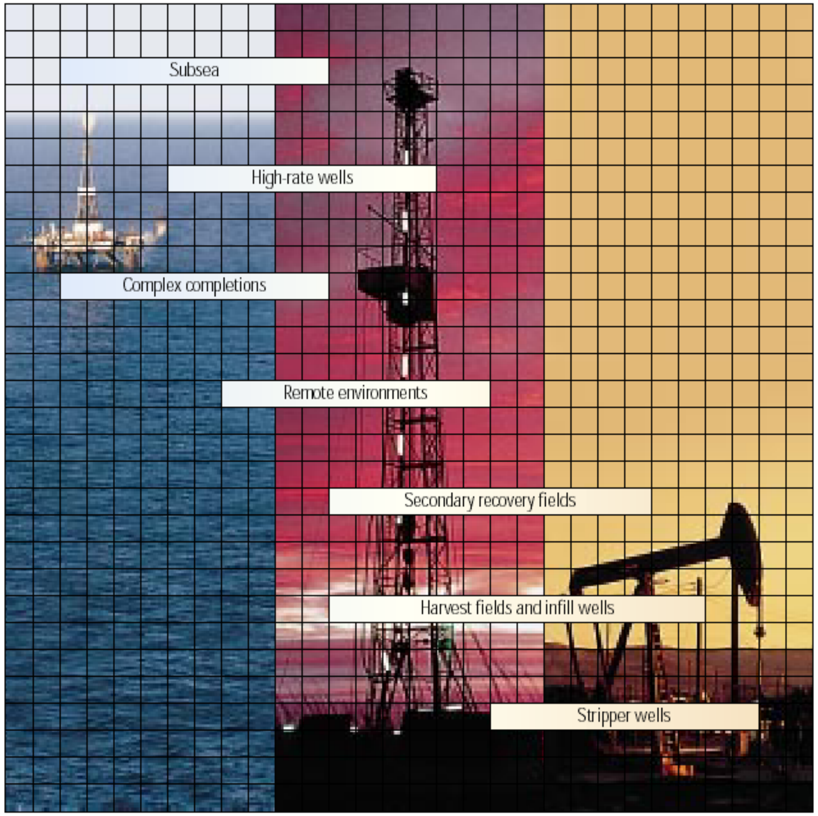
Design
of "smart" polymer systems



Two different applications in oil recovery:

- Blocking water in the well
- Fracturing

Design
of “smart” polymer systems



Two different applications in oil recovery:

- Blocking water in the well
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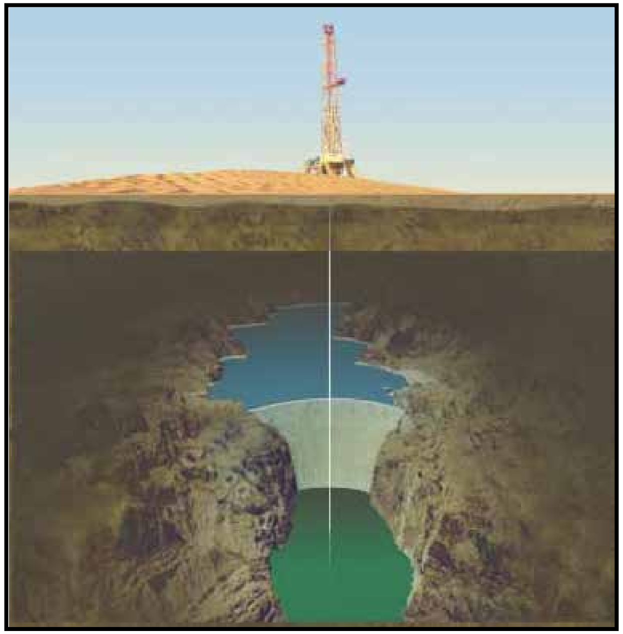
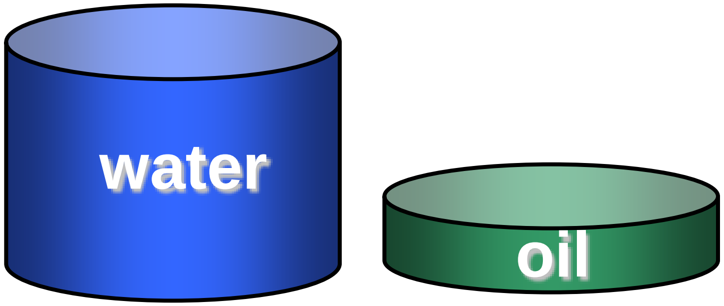
The importance of limiting the water influx

World average from producing oil fields:



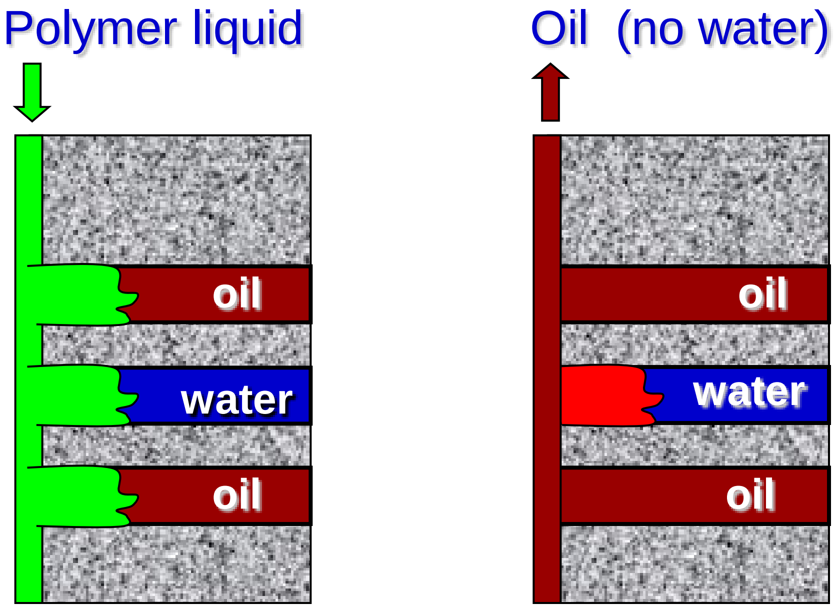
3 tons of water
per
1 ton of oil



More than **40 bln. dollars** are spent annually for extraction and recovery of water that nobody needs

Smart polymers for limiting water influxes

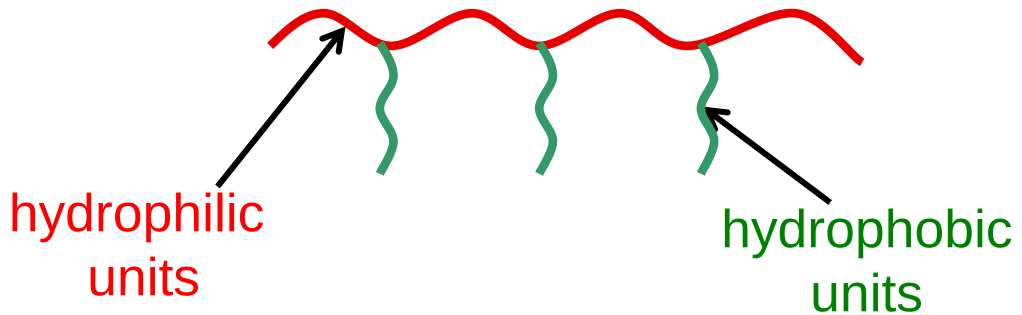
The main aim of the work is
to develop smart polymer materials that find the water inflow by themselves and block it

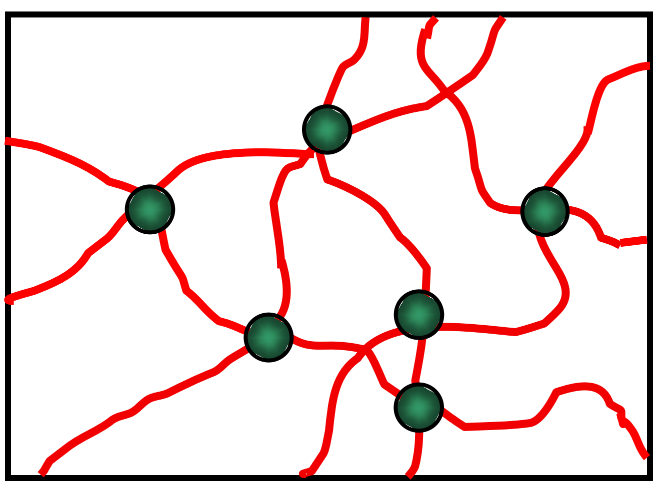


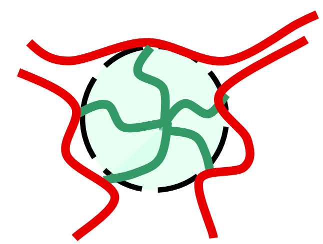
These materials should:

- have low viscosity at injection
- form a gel in contact with water
- keep low viscosity in contact with oil

Hydrophobically associating polymers



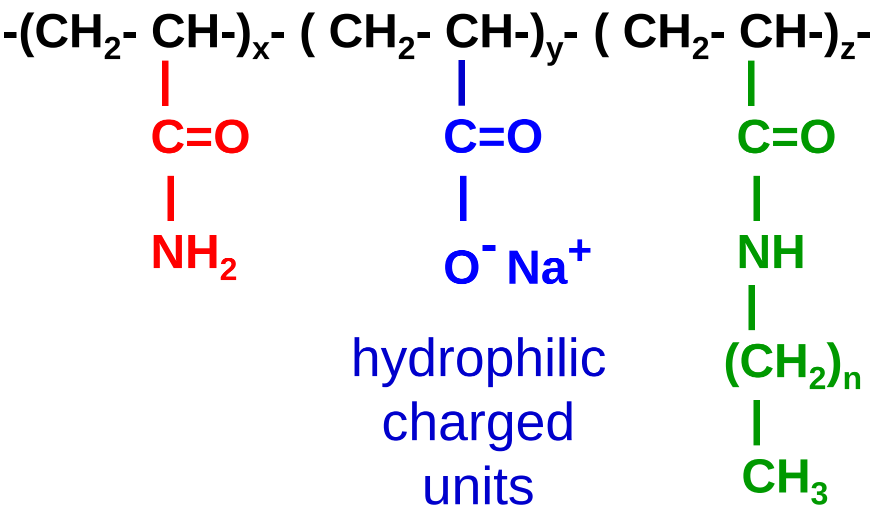

Physical gel


Hydrophobic aggregate

Polymer composition

3 types of units

M_w= 1 000 000



hydrophilic
charged
units

hydrophilic
non-charged
units

hydrophobic
units

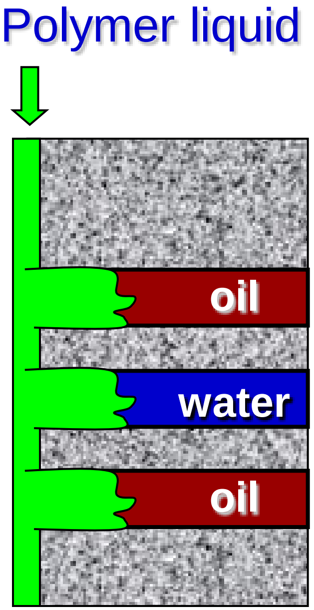
0-20 mol.%

0-3 mol.%

n = 8, 11

How to apply the polymer system for limiting water influx?

Thus, the optimum composition of hydrophobically associating polymer, which gives rather strong gel, was determined.

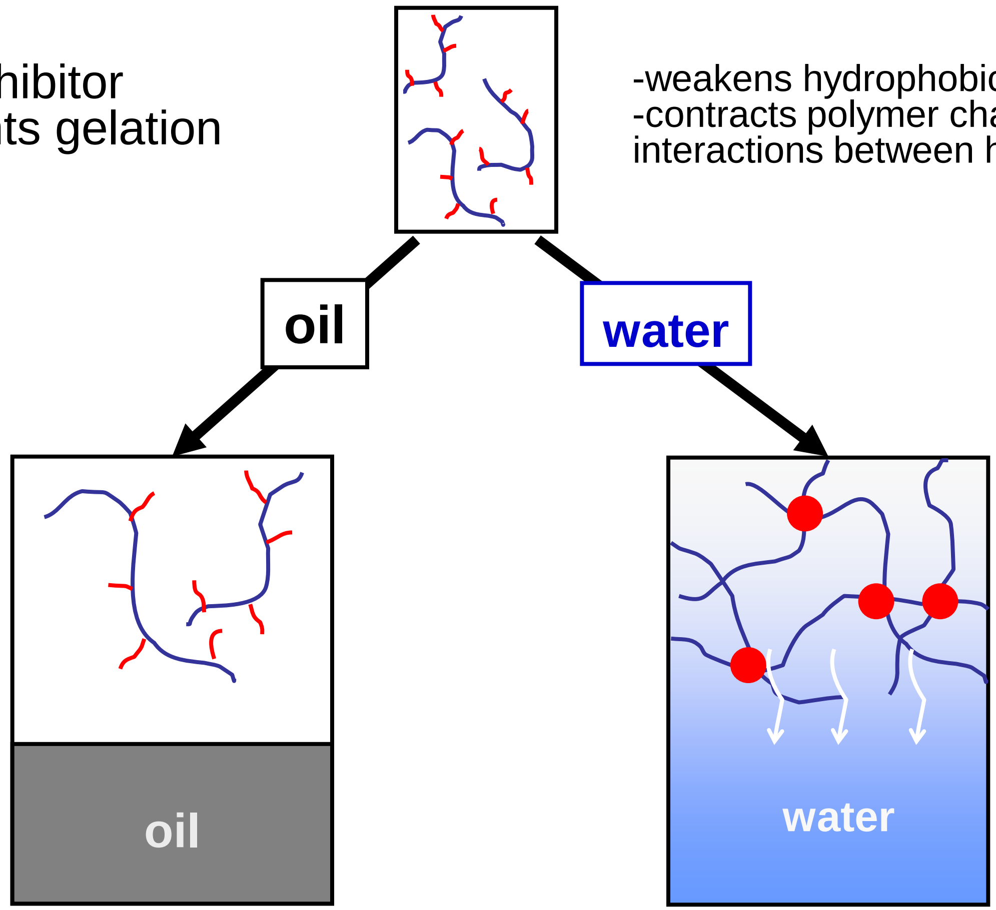


- If we will just pump in the well aqueous solution of hydrophobically associating polymer, it will form physical gel in the whole well volume
- The gel will block not only the flow of water, but also the flow of oil

How to make a smart system?

inhibitor
prevents gelation

-weakens hydrophobic interactions,
-contracts polymer chains thus further reducing interactions between hydrophobes



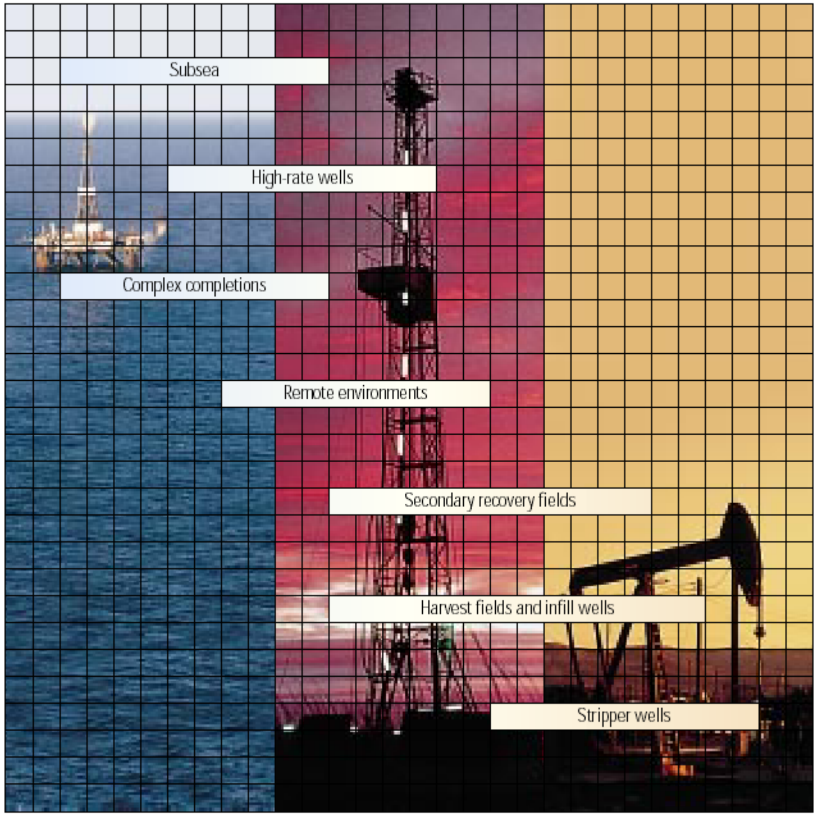
No gel plug –

inhibitor insoluble in oil remains in polymer solution

Gel plug –

inhibitor soluble in water is removed from polymer solution

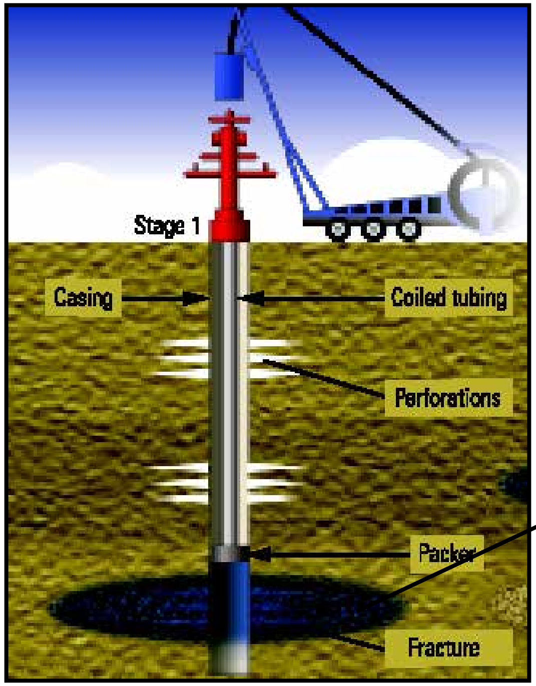
Design
of “smart” polymer systems

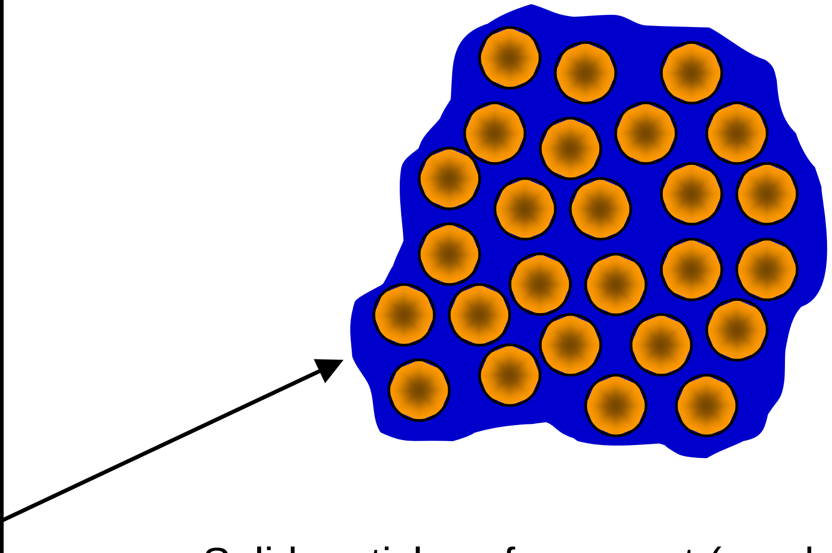


Two different applications in oil recovery:

- Blocking water in the well
- Fracturing

Fracturing fluids

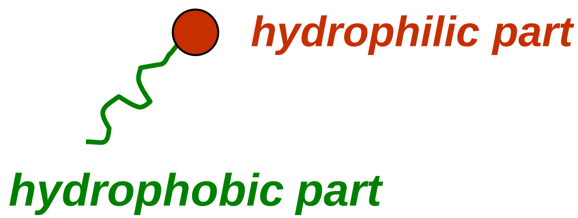


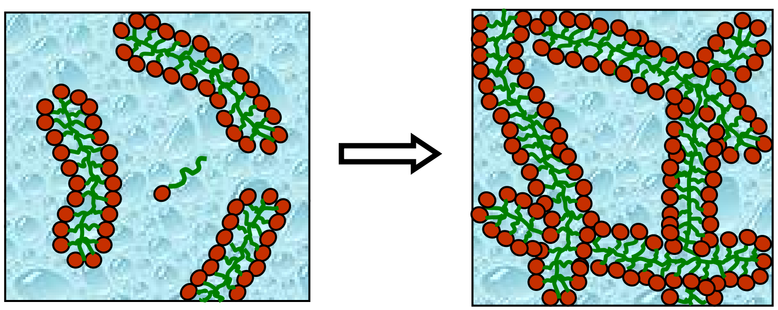


Solid particles of proppant (sand or ceramics) suspended in highly viscous medium.

- Fracturing fluids are used to create and to fill up the artificial fractures in oil layer. This artificial system has a high permeability with respect to oil in comparison with the rock.

Viscoelastic surfactants



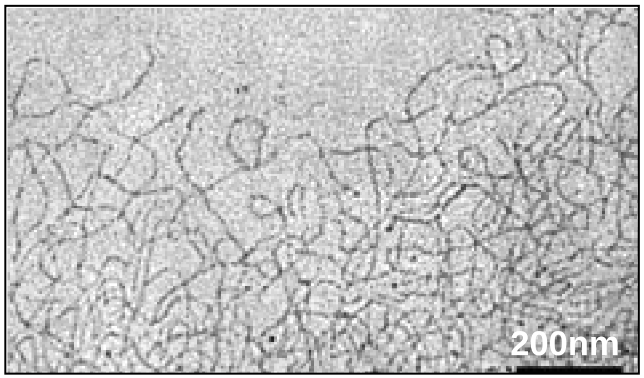


cylindrical micelles

network

Cryo-TEM images of 4.5 wt% potassium oleate aq. solution in the presence of 2% KCl

C. Flood, C.A. Dreiss et al. // Langmuir. 2005, v.21, p.7646.



VES form enormously long cylindrical micelles in water.

These micelles can entangle with each other, forming transient networks that exhibit viscoelastic behavior.

Viscoelastic surfactants

Cationic surfactant J508

Erucyl bis(2-hydroxyethyl)methylammonium chloride

$$
\begin{array}{c}
CH_2CH_2OH \\
| \\
C_8H_{17}-CH=CH-C_{12}H_{24}-N^{+}-CH_3 \quad Cl^{-} \\
| \\
CH_2CH_2OH
\end{array}
$$

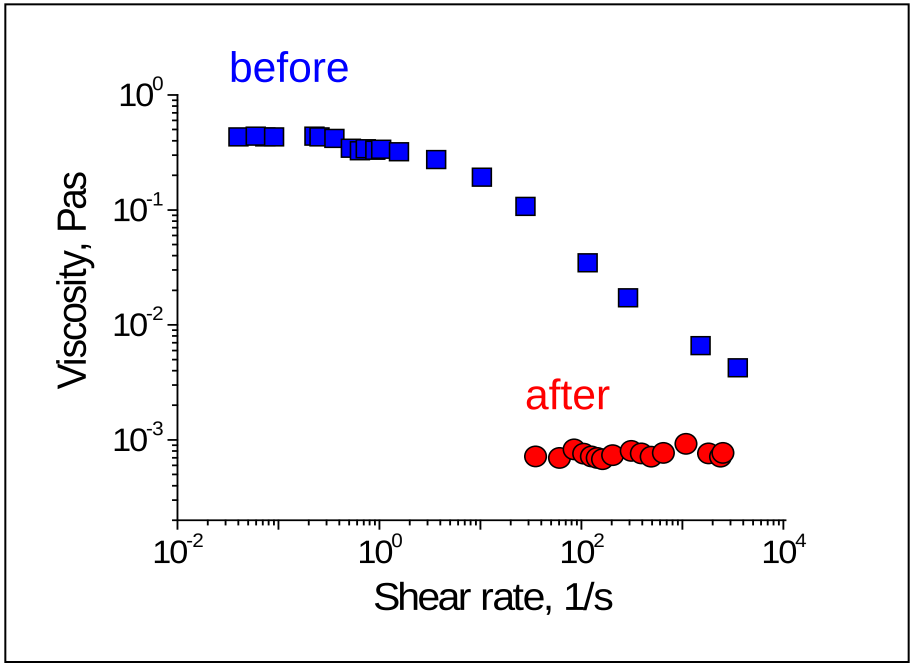
Anionic surfactant

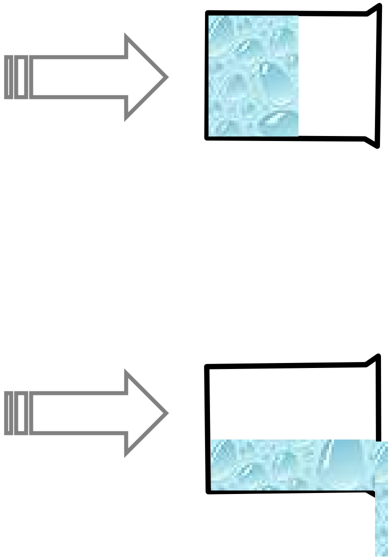
Potassium oleate

$$C_8H_{17}-CH=CH-C_8H_{16}-COO^{-} \quad K^{+}$$

Effect of hydrocarbon Rheology

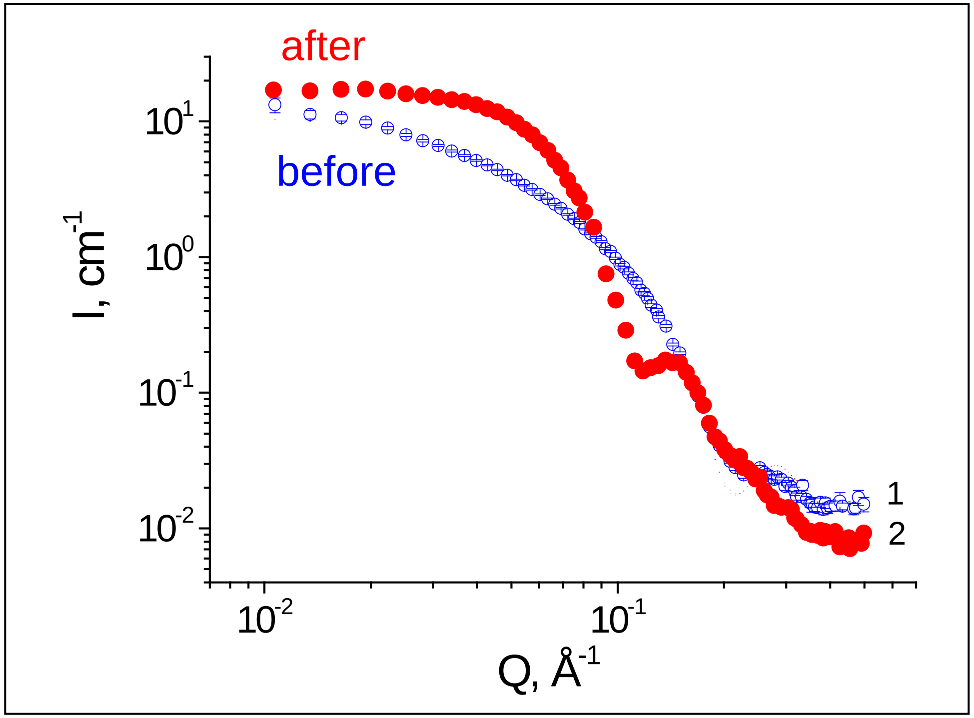
Potassium oleate: 0,4 wt.%
Solvent: 6 wt.% KCl in water **20^{0}C**

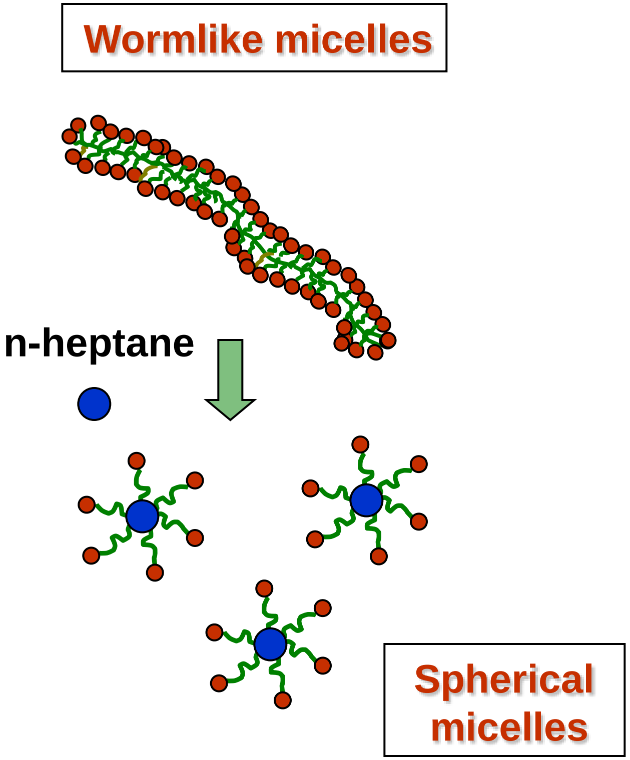




- Contact with hydrocarbon induces the decrease of viscosity of VES by 5 orders of magnitude.

Effect of hydrocarbon
SANS

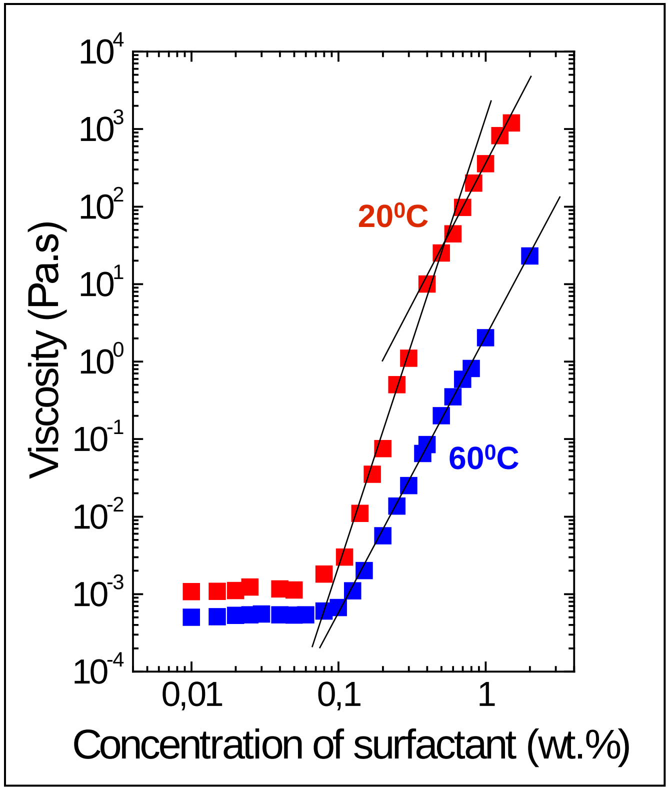


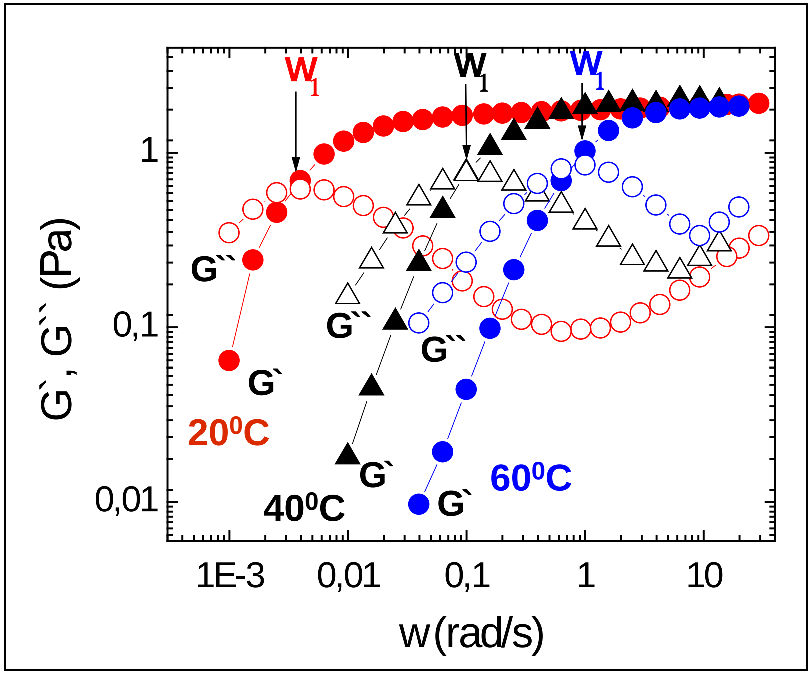


- Contact with hydrocarbon induces the transition of wormlike micelles into spherical ones leading to the disruption of the network.

Effect of temperature

Solvent: 3 wt.% KCl in water





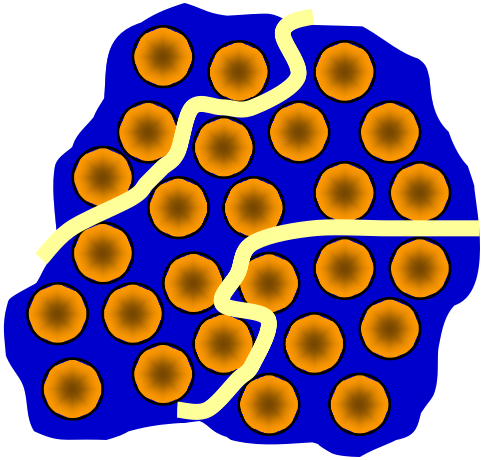
$h = G_0 \cdot t$

$t = 1/w$

$G''_{мин} / G_0 \; » \; l / \bar{L}$

- Heating from 20 to 60^0C leads to drop of viscosity by 2 orders of magnitude, which may be due to shortening of micellar chains

Viscoelastic surfactant for fracturing fluids



Advantage of VES used for fracturing fluids:

- responsiveness to hydrocarbons

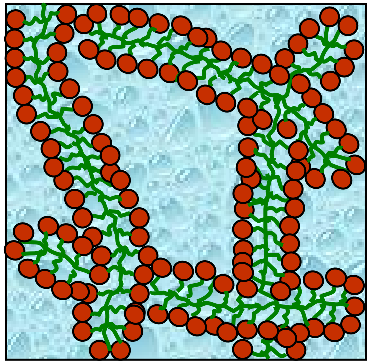
It is especially important at the stage, when the porous space between proppant particles should be cleaned up to allow oil to drain to the well.

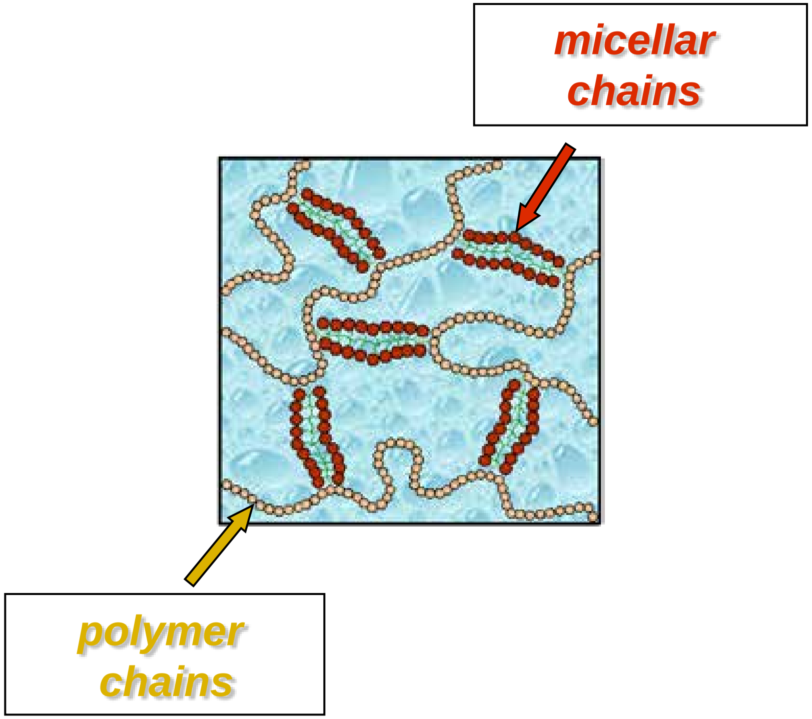
Disadvantages of VES viscosifiers:

- high cost,
- drop of viscosity at elevated temperatures taking place in subterranean reservoirs

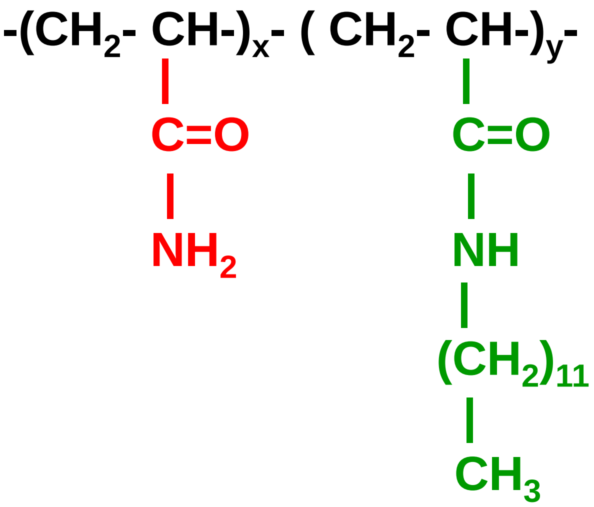
.

Strengthening of the network by added polymer





Polymer



hydrophilic uncharged units

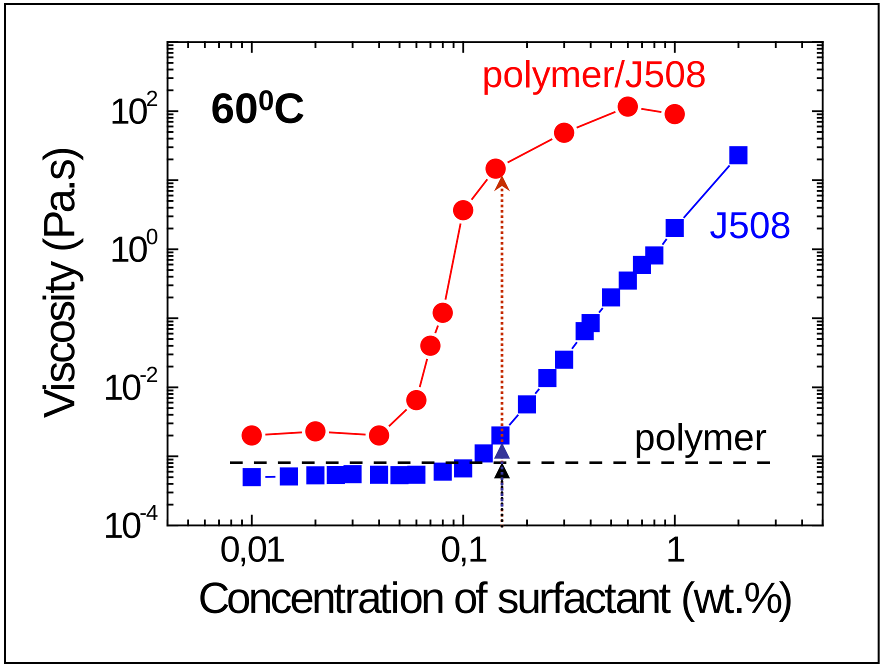
hydrophobic units

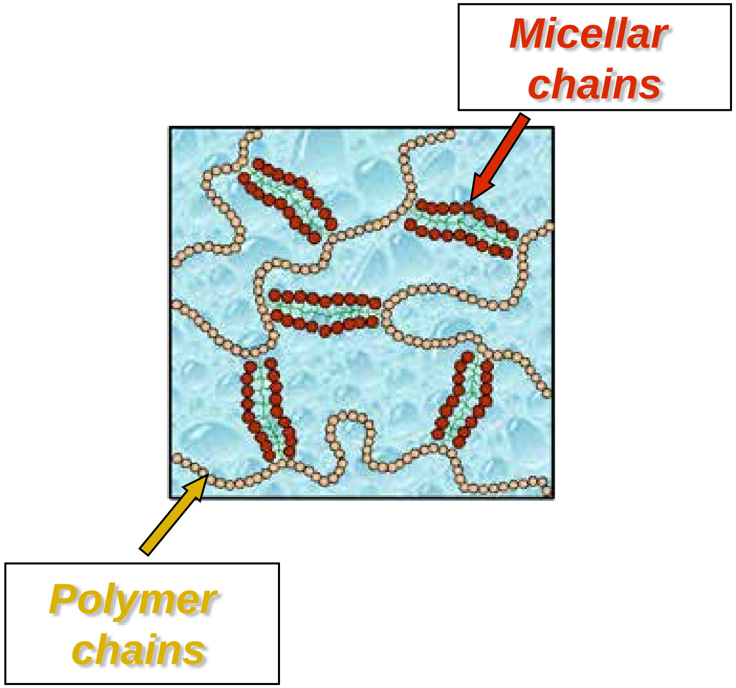
0.1-0.2 mol.%

M_w=800 000 g/mol

Viscosity enhancement

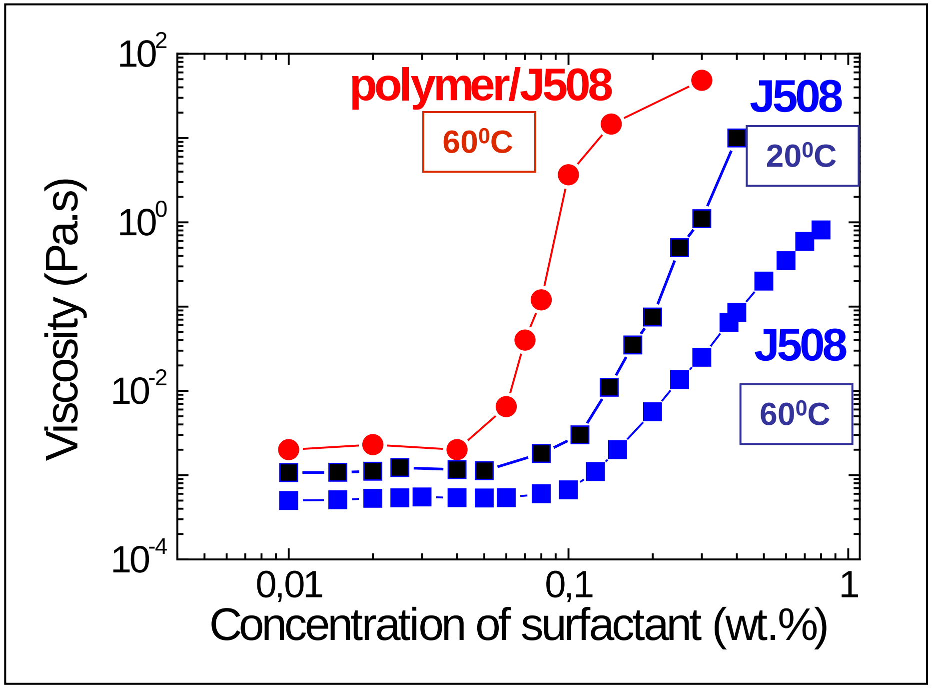
*Polymer **0,2-C12**, concentration:* 0,5 wt.%
Solvent: 3 wt.% KCl in water





• The viscosity of polymer/surfactant system becomes by 4 orders of magnitude higher than the viscosity of polymer or surfactant taken separately.

Effect of temperature

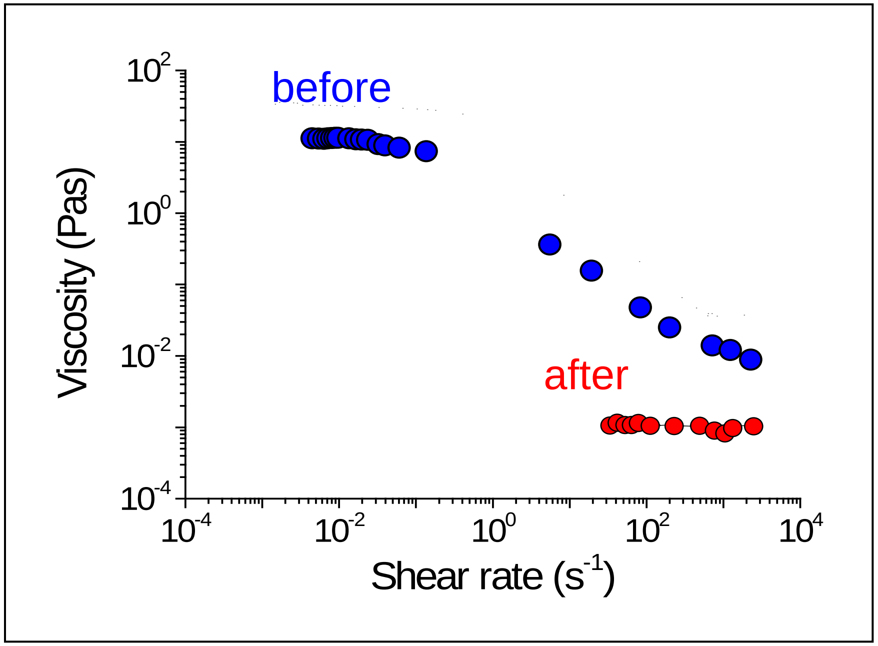


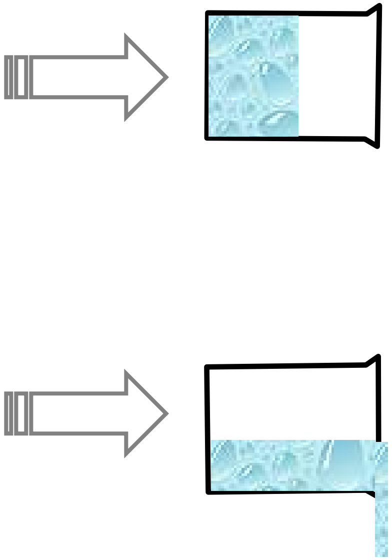
Polymer ***0,2-C12****,*
concentration: 0,5 wt.%
Solvent: 3 wt.% KCl in water

- Polymer/surfactant system is much more stable to heating, and at 60 ^{0}C it has much higher viscosity than surfactant alone at 20 ^{0}C. This is due to the fact that polymer chains do not break and recombine like VES micelles

Sensitivity to hydrocarbon
Rheology

Polymer ***0,2-C12*** *: 0,5 wt.%*
Potassium oleate : 0,4 wt.%
Solvent: 6 wt.% KCl in water

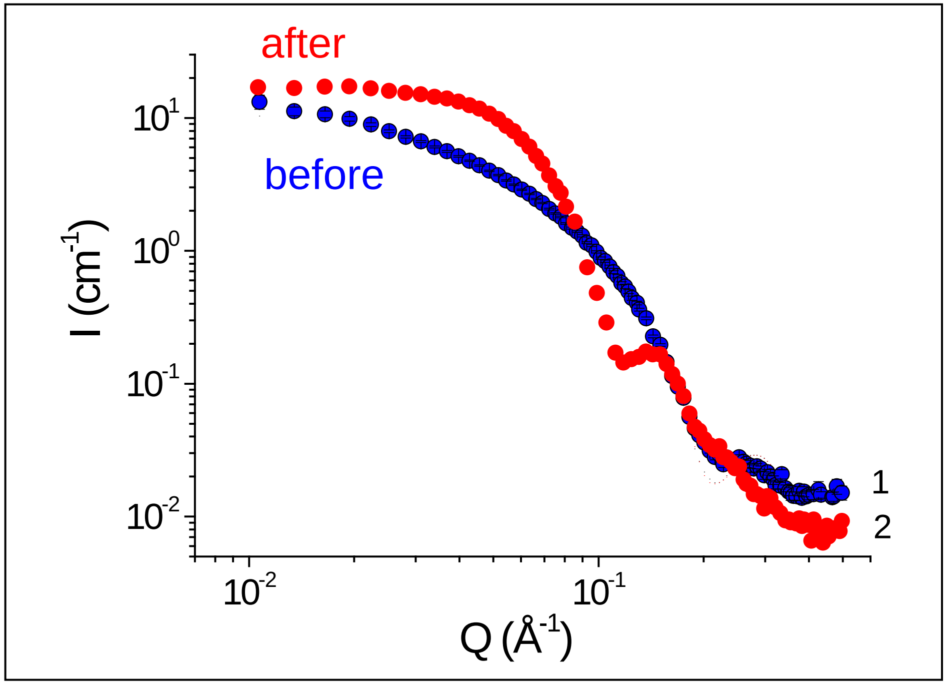


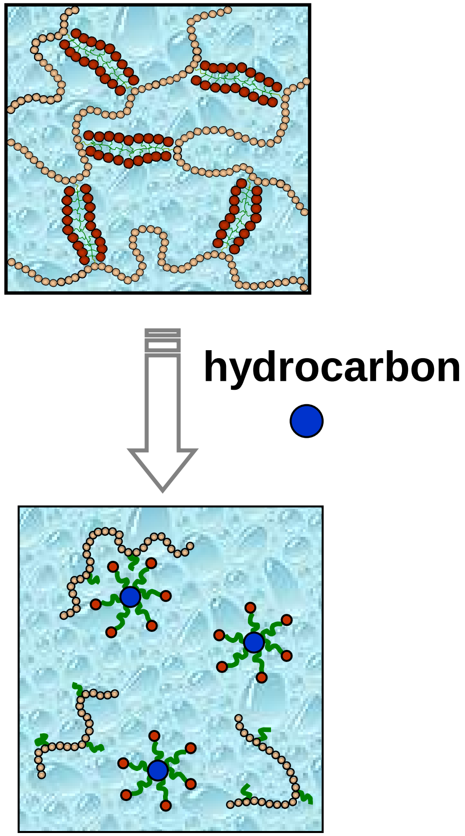


- Hydrocarbon induces the drop of viscosity by 3-4 orders of magnitude

Sensitivity to hydrocarbon SANS

*Polymer **0,2-C12** : 0,5 wt.%*
Potassium oleate : 3 wt.%
Solvent: 6 wt.% KCl in water





- Hydrocarbon induces the transition of wormlike micelles into spherical ones thus leading to the disruption of the whole network.

Which polymers are the smartest ?

→ Living systems

They can perform much more complex and diverse functions, than any artificially designed systems.

Biomimetic approach: to study how biopolymer structures are designed in living systems and to realize analogous types of self-organisation for synthetic polymer systems

Design of sequences in copolymers

Unique spatial structure of many biopolymers (for example, globular proteins) is defined by the sequence of monomer units in the chain.

Can we reach the same self-organisation for synthetic copolymers, by “regulating” their sequences of monomer units ?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Conformation-Dependent Design of Sequences in Copolymers I
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ADVANCES IN POLYMER SCIENCE
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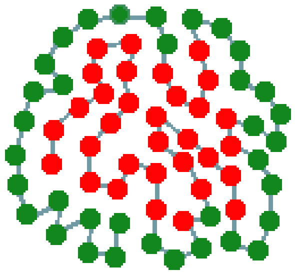
ADVANCES IN POLYMER SCIENCE
Volume Editor A. R. Khokhlov
Conformation-Dependent Design of Sequences in Copolymers II
Conformation-Dependent Design
Springer

Globular proteins - enzymes

1. Are <u>soluble</u> in aqueous media

2. Adopt the <u>globular state</u> in aqueous media



For <u>homopolymers</u> and <u>random copolymers</u> these requirements contradict to each other

<u>Hydrophobic</u> A-units (red) form the dense core of the globule, while <u>hydrophilic</u> B-units (green) - constitute the stabilizing envelope for the core.

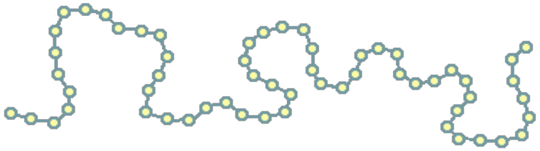
<u>Question</u>: is it possible to design such an AB-sequence of a synthetic copolymer, so that in its most dense globular conformation all A-units would be in the core of the globule, and all B-units would form the envelope of this core ?

→ protein-like AB-copolymers

Khokhlov A.R., Khalatur P.G. Physical Review Letters, 1999, 82(17), 3456

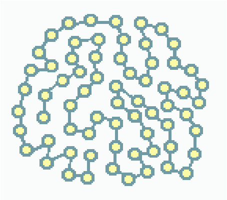
Computer realization of protein-like AB-copolymers

Stage 1



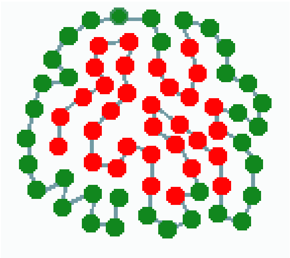
Homopolymer coil with excluded volume.

Stage 2



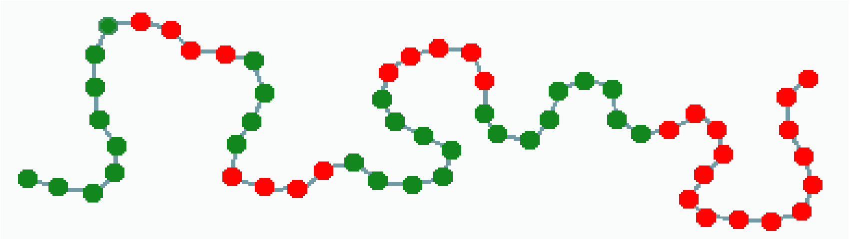
The strong attraction of links is switched on. The homopolymer globule is formed.

Stage 3

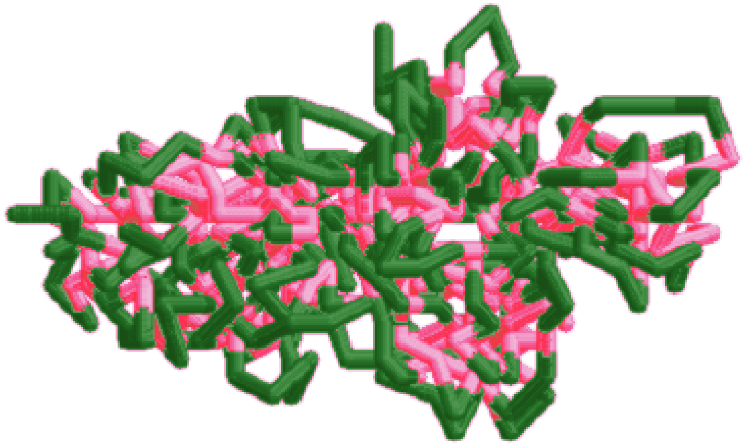


“Instant photo” of the globule is considered. Links on the surface are colored in green and called hydrophilic. Links in the core are colored in red and called hydrophobic. Then the primary structure is fixed.

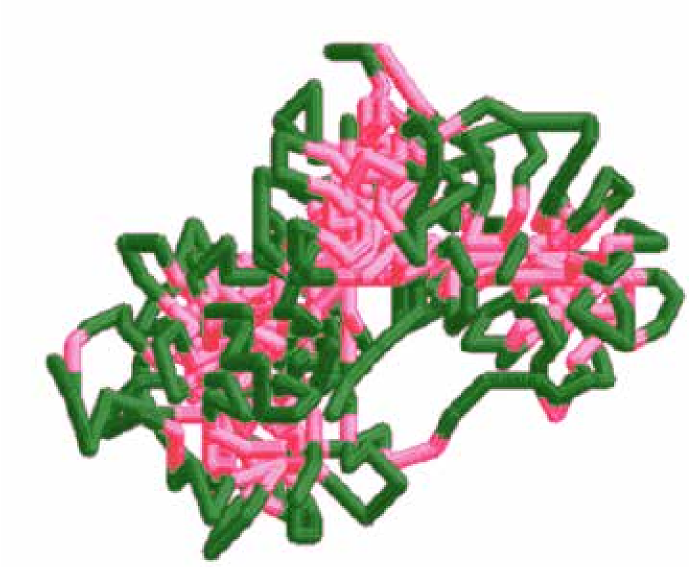
Stage 4



The uniform strong attraction is removed and different interaction potentials are introduced for green and red links. The protein-like copolymer is ready.



Random copolymer $\langle R_g^2 \rangle_{core}$= 106.6

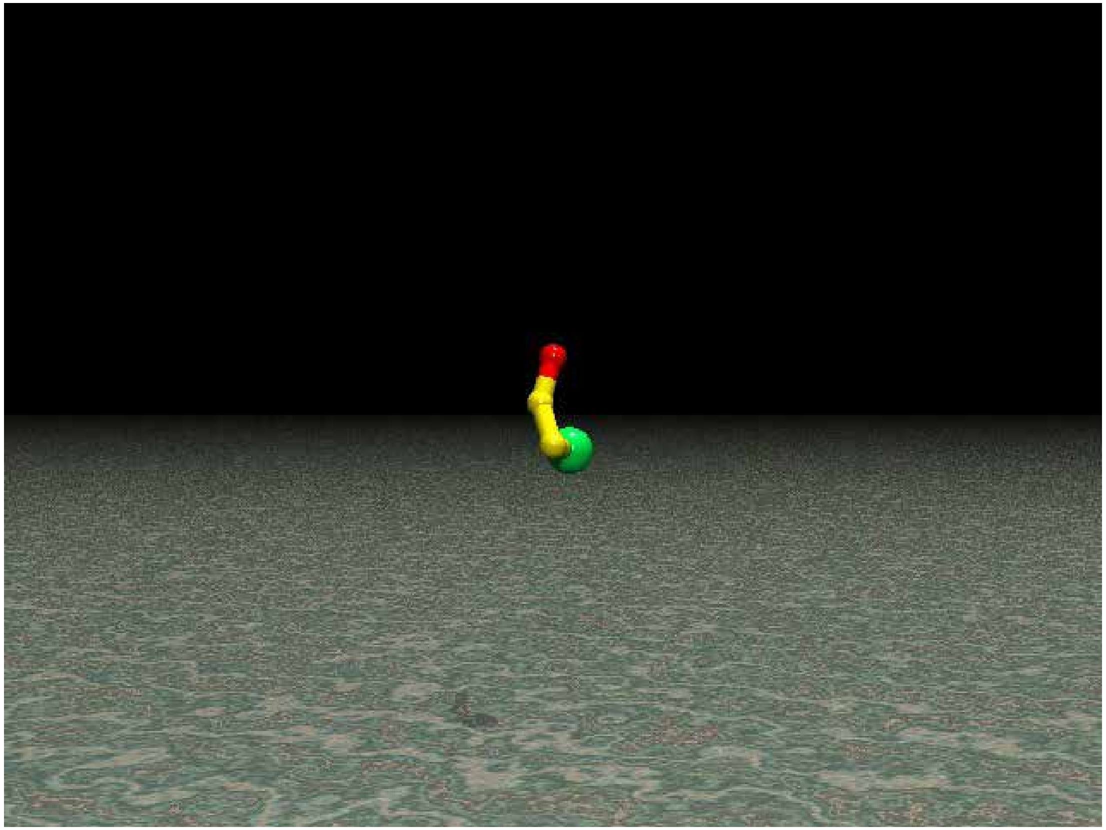


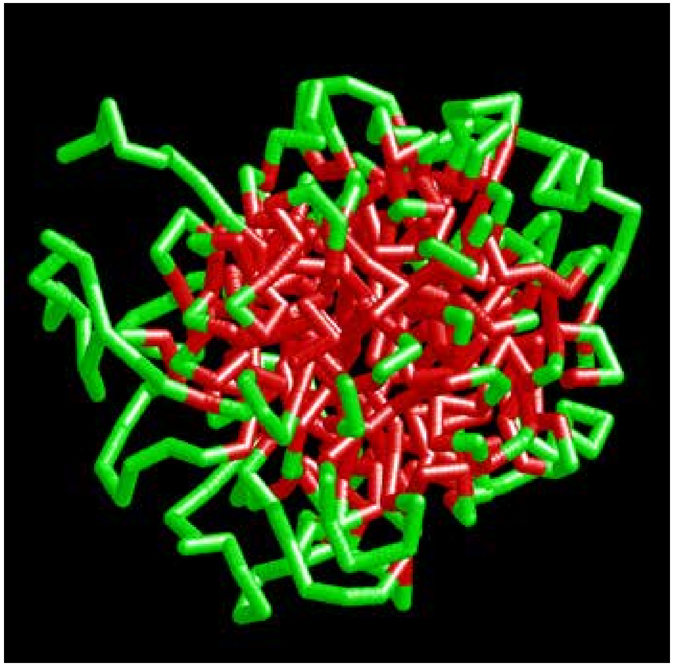
Random-block copolymer $\langle R_g^2 \rangle_{core}$=99.4

Protein-like copolymer

$\langle R_g^2 \rangle_{core}$=74.1

Copolymerization with simultaneous globule formation

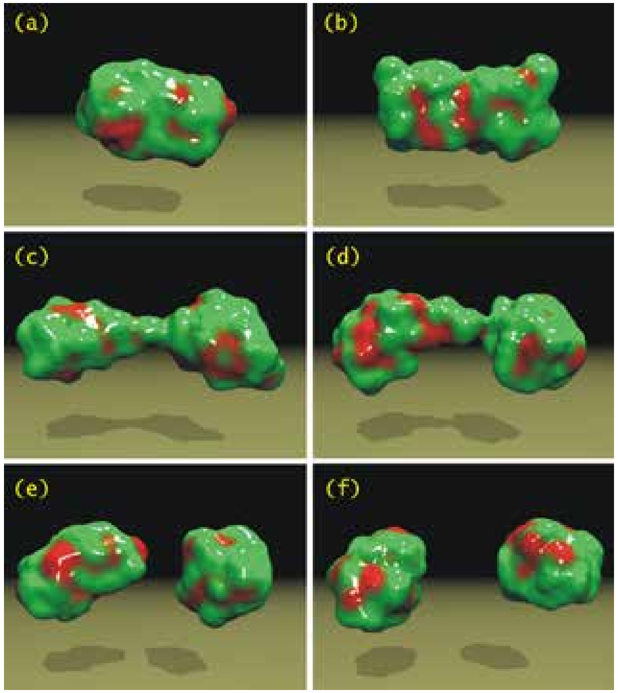


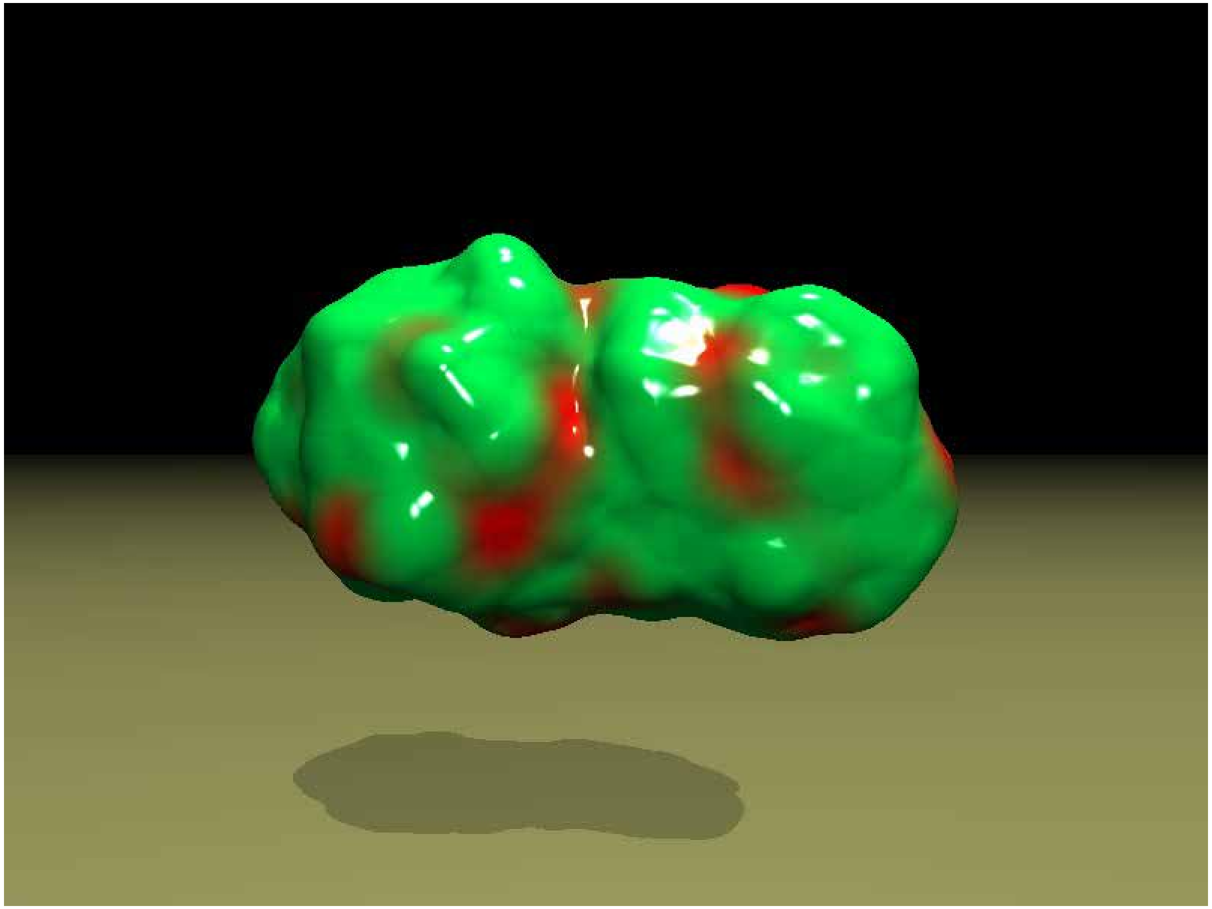


Berezkin A.V., Khalatur P.G., Khokhlov A.R. J. Chem. Phys., 2003, 118, 8049

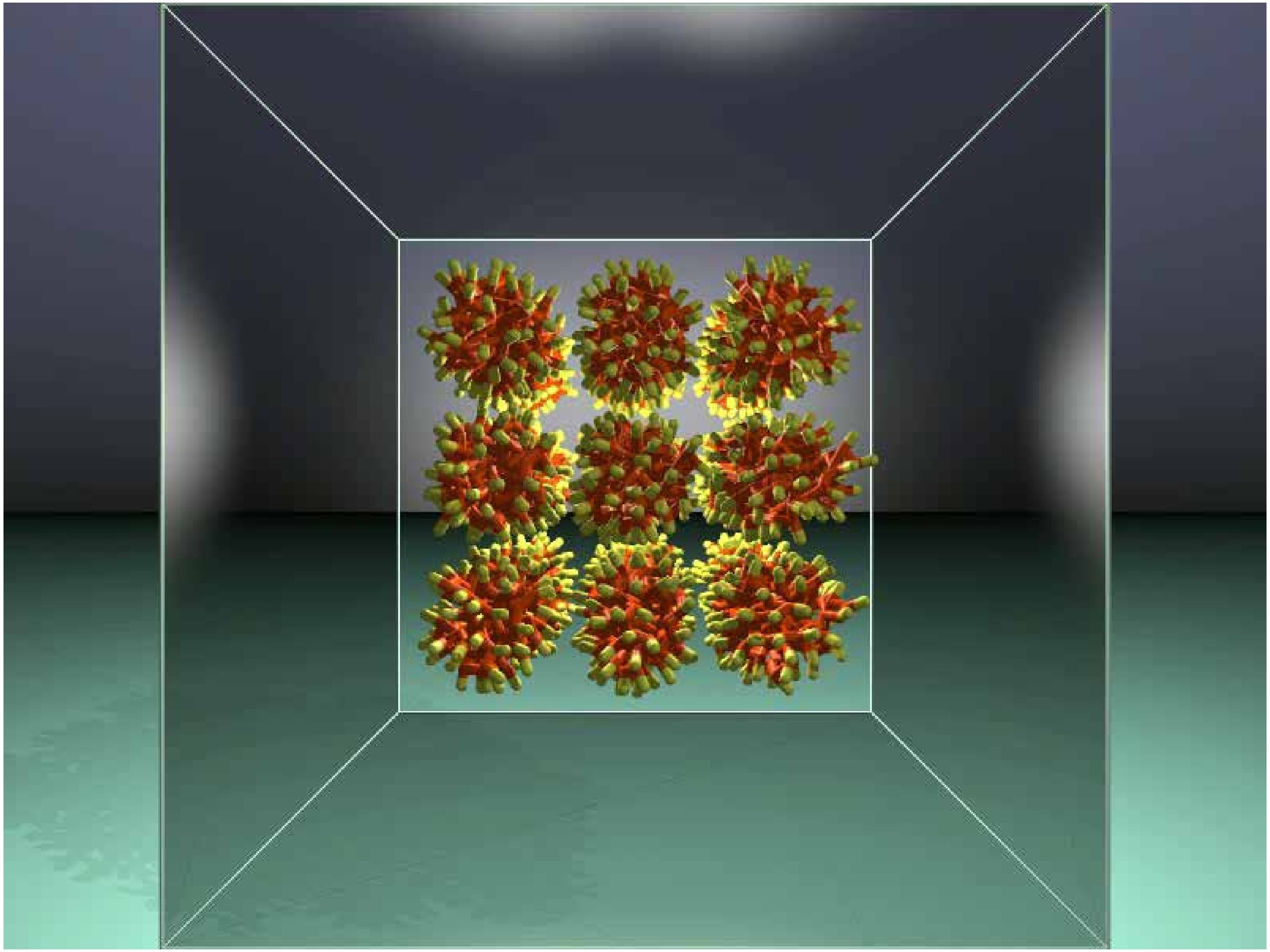
Stabilization vs. Aggregation

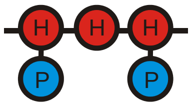
Two proteinlike globules at poor solvent conditions





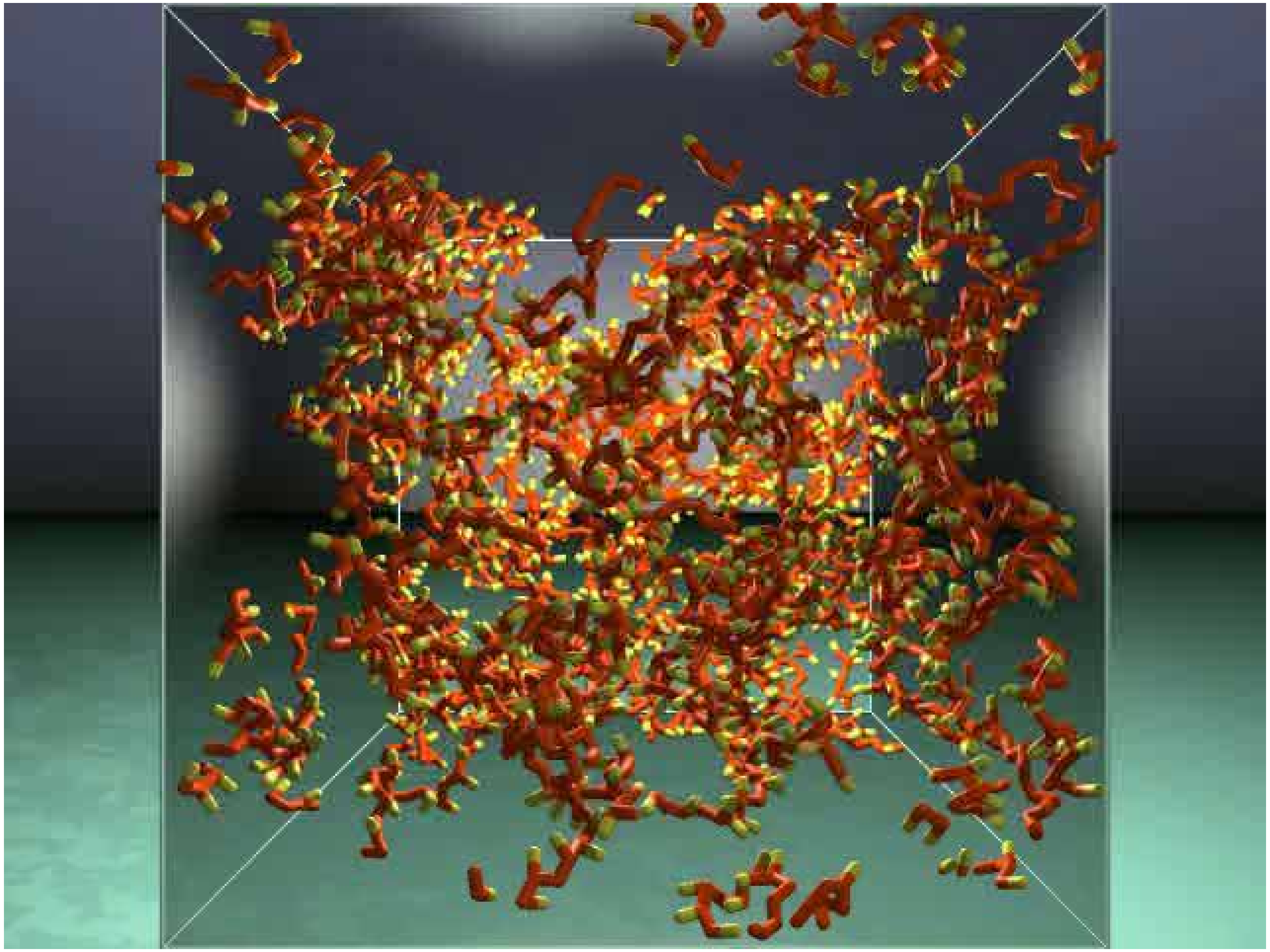
System of m=27 proteinlike HA copolymers does not show tendency to aggregation

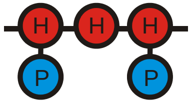




THERMOREVERSIBILITY for protein-like HA copolymer

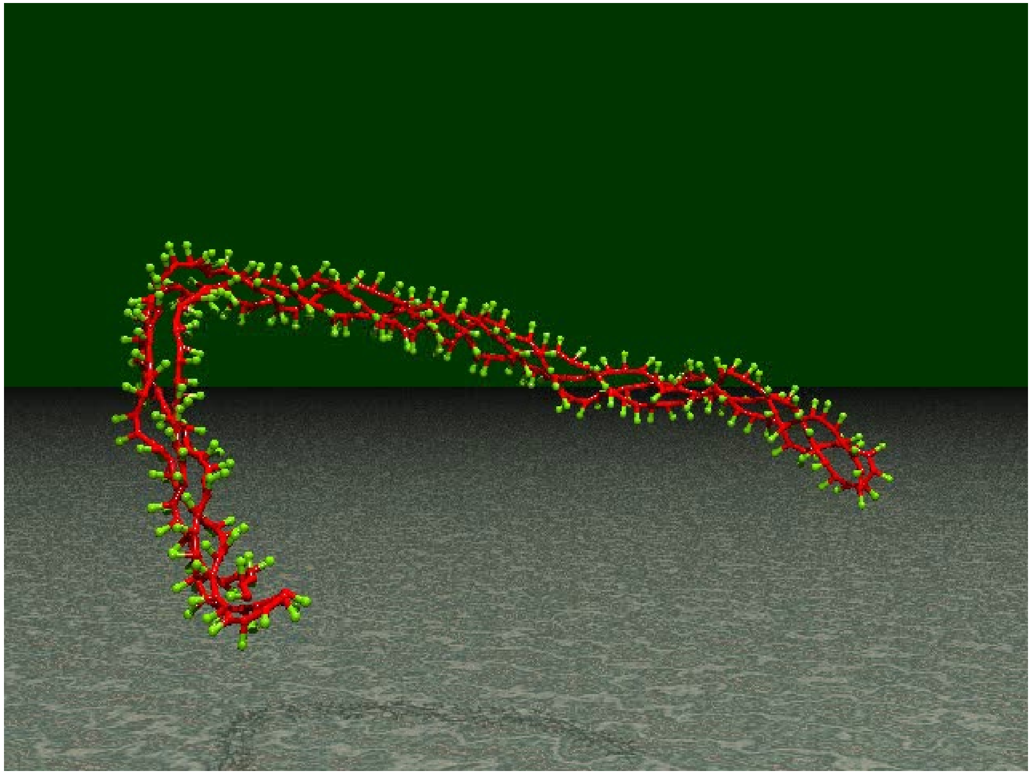
Heating to T=4 and cooling back to T=1

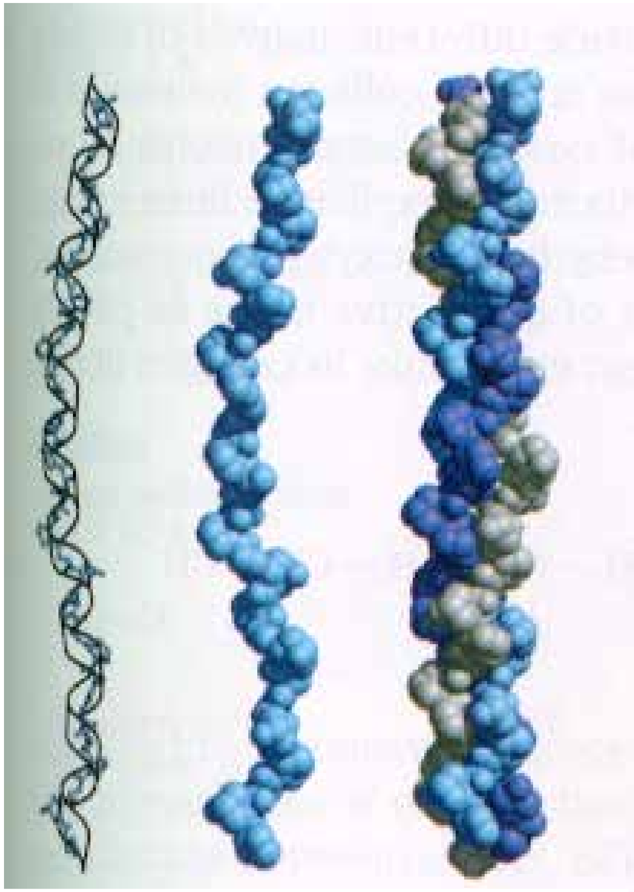




About 20% of globules form aggregates

Collagen-like globule

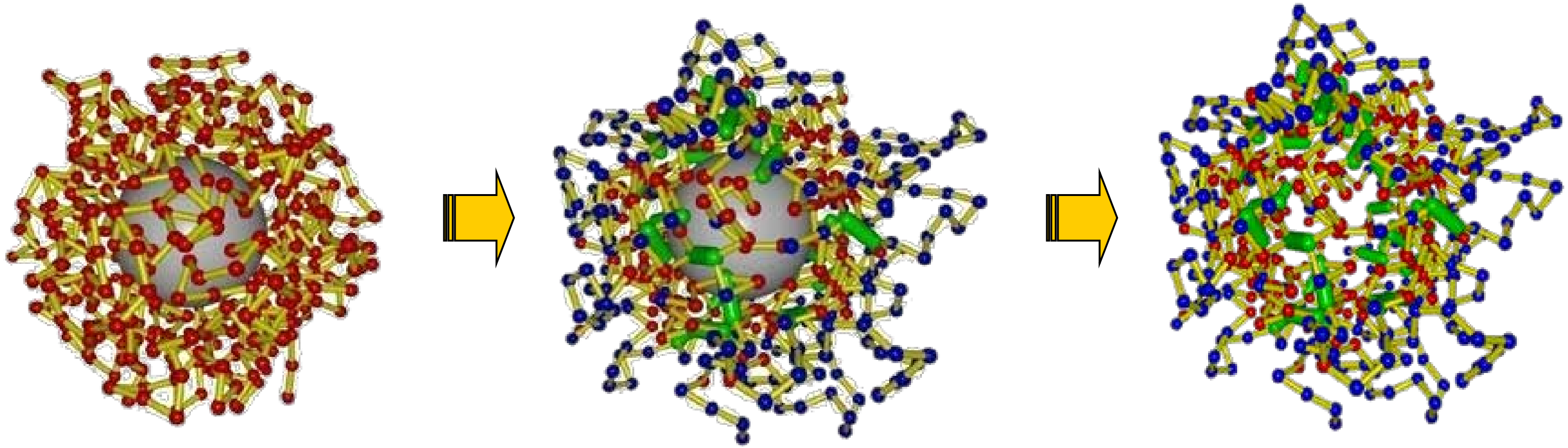




Molecular Dispensers

Envelope Preparation Scheme

- Polymer chain adsorbs onto the particle
- Coloring of polymer chain
- Introduction of junctions between hydrophilic or hydrophobic monomer units.
- Particle removal

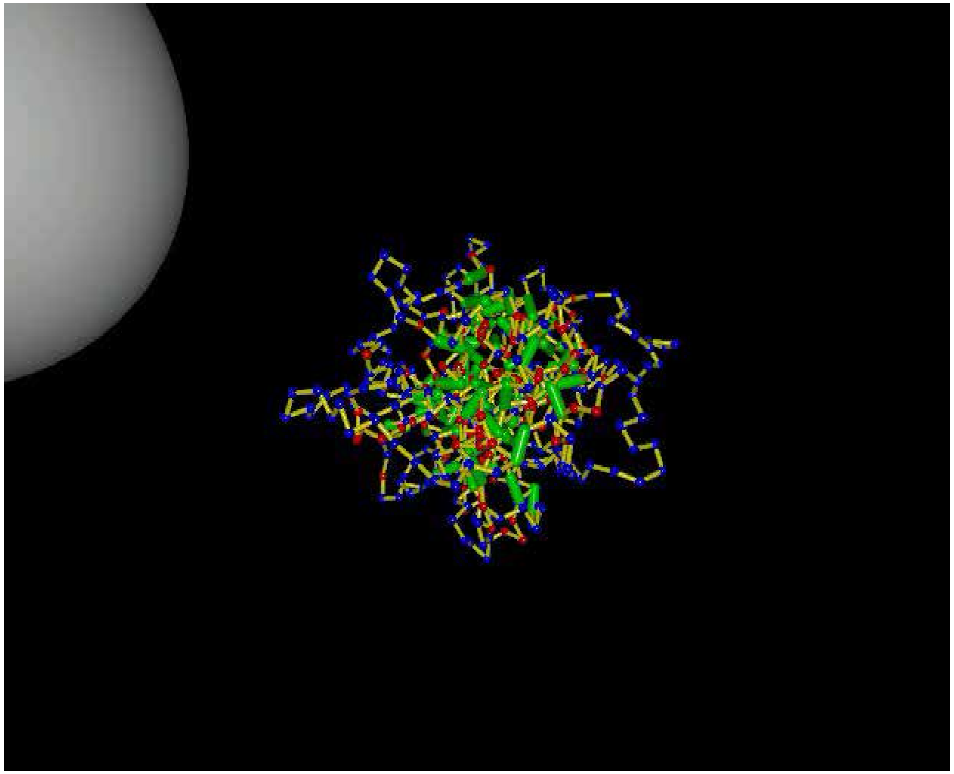


Velichko Yu.S., Khalatur P.G., Khokhlov A.R. Macromolecules, 2003, 36(14), 5047

Molecular Dispensers

Copolymer-Particle Interaction

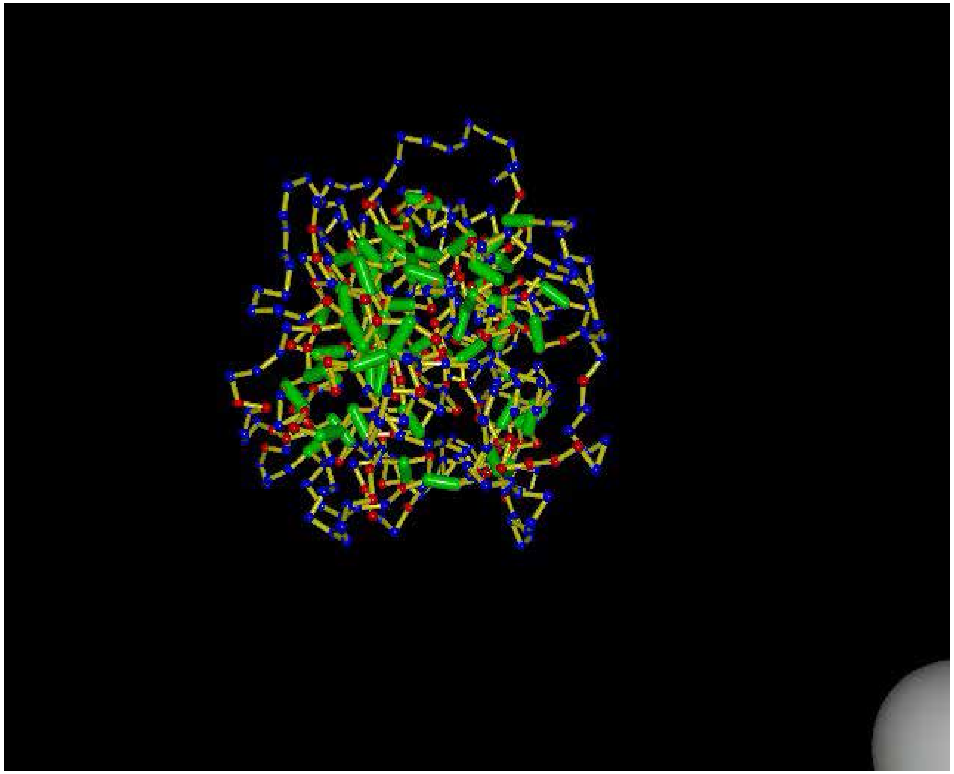
(particle's size = parental particle size)



Molecular Dispensers

Copolymer-Particle Interaction

(particle’s size > parental particle size)



Concept of Evolution in Polymer Science

- Biopolymers (proteins, DNA, RNA) possess complicated sequences of monomer units which encode their functions and/or structure.
- These sequences should be statistically different from random ones, primarily from the viewpoint of information content.
- On the other hand, first copolymers at the very beginning of molecular evolution can be only random (zero information content).

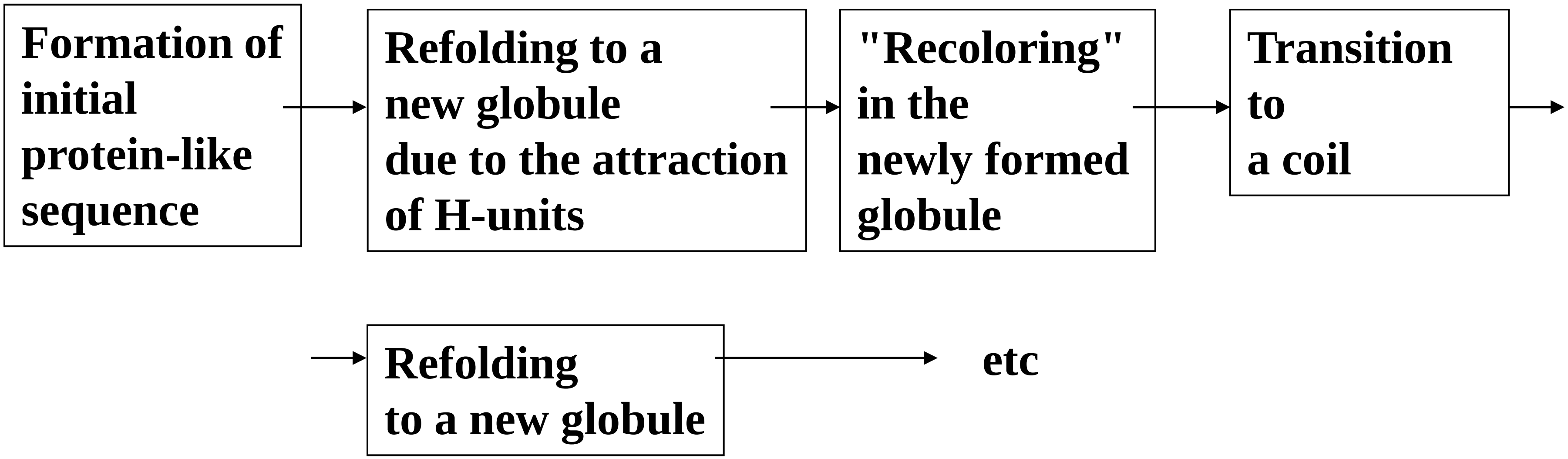
Question: how to describe the increase of information complexity of copolymer sequences in the course of molecular evolution

Since information content is a mathematically defined quantity, this question is quantitative.

Because of the lack of information on the early prebiological evolution, this question is very difficult. Therefore, of particular interest are "toy models" of evolution of sequences which show different possibilities of appearance of statistical complexity in the sequence.

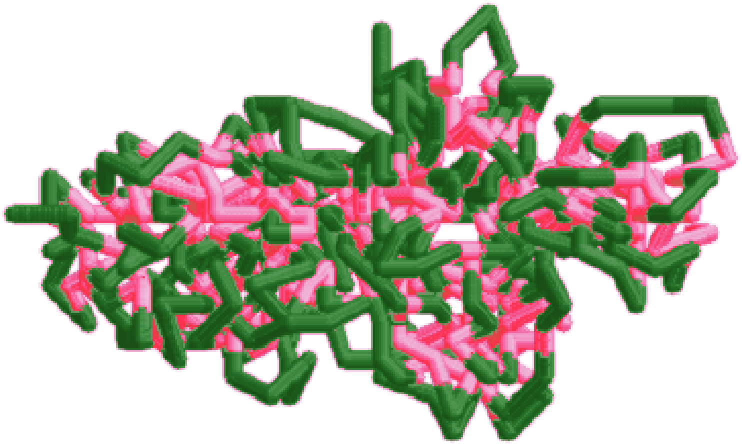
This can be achieved via coupling of polymer chain conformation and evolution of sequences.

How to introduce explicitly the concept of evolution of sequences into the scheme of generation of protein-like copolymers ?



As a result, we obtain some evolution of sequences which depend on the interaction parameters of the refolding process.

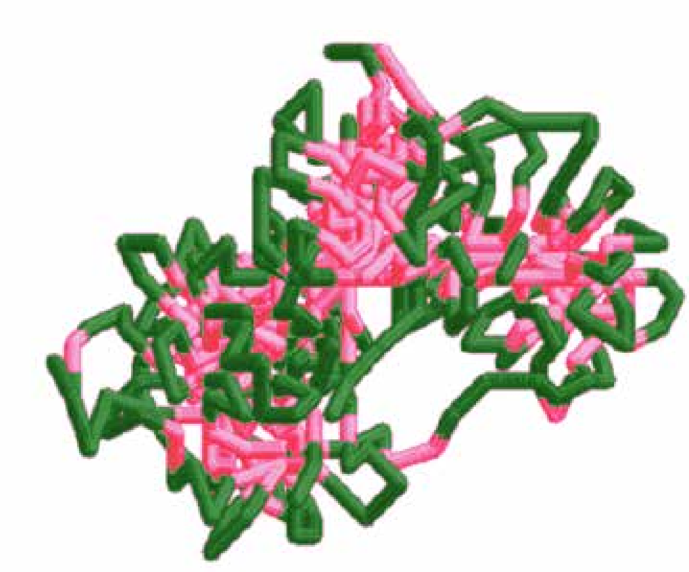
Question: whether this evolution leads to the increase of complexity (ascending branch of the evolution) or we will end up with some trivial sequence (descending branch of the evolution)?



Random copolymer $\langle R_g^2 \rangle_{core}$= 106.6

Protein-like copolymer

$\langle R_g^2 \rangle_{core}$=74.1

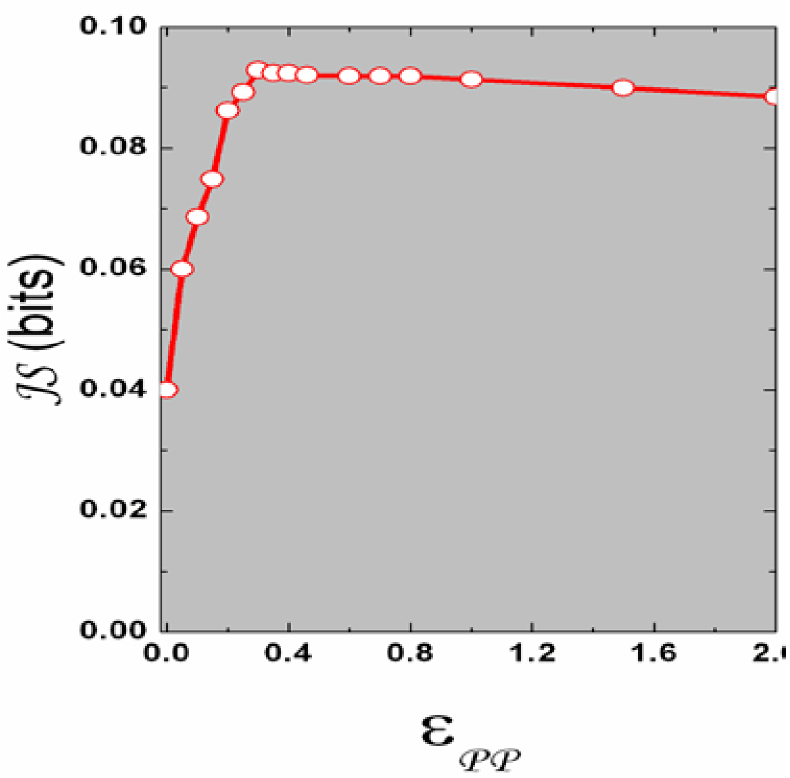


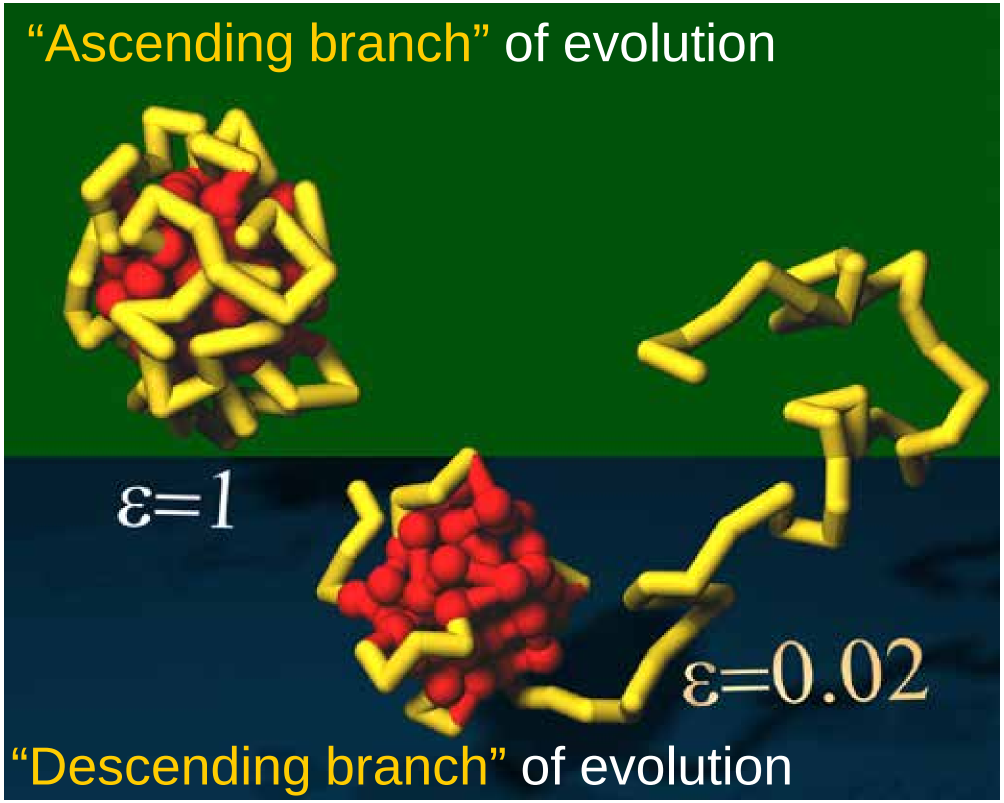
Random-block copolymer $\langle R_g^2 \rangle_{core}$=99.4

"REPEATED COLORING" =

coloring + equilibration (Molecular dynamics) + new coloring + … etc.

$e_{HH} = 2kT$; $e_{PP} = \varepsilon$ is variable (in kT units)

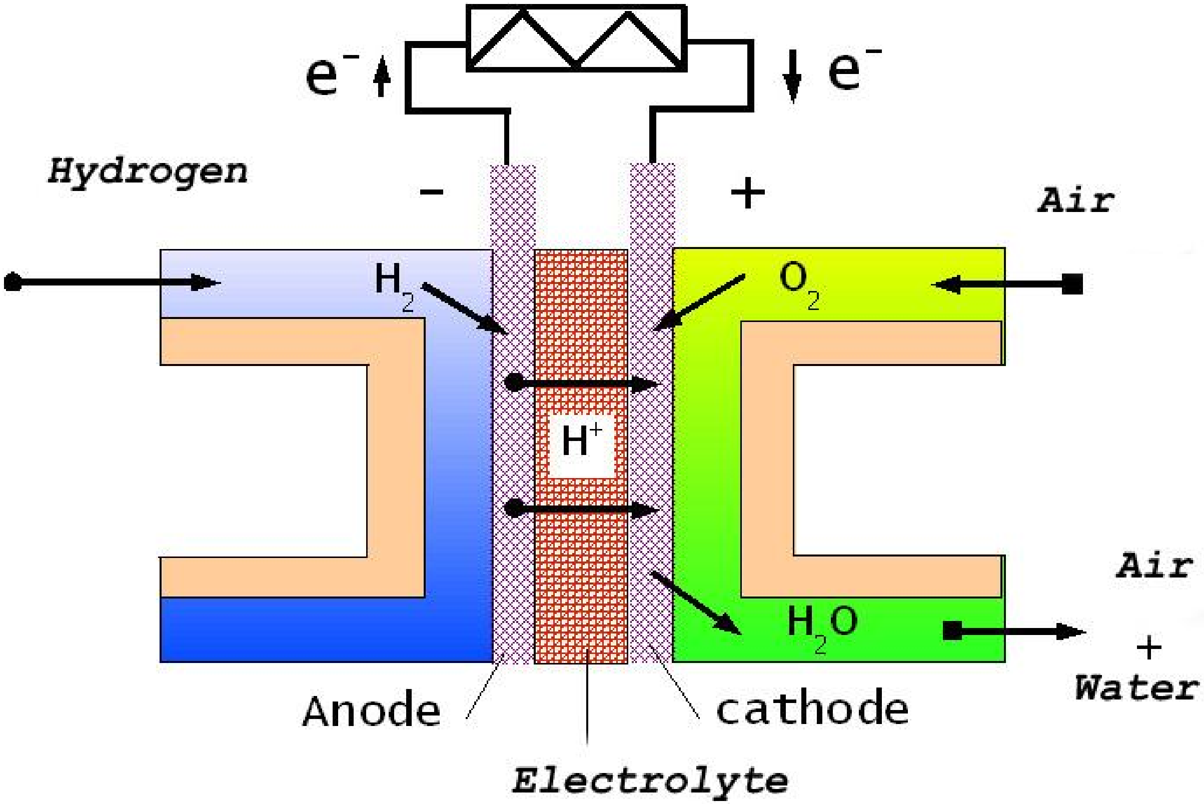




Khalatur P.G., Novikov V.V., Khokhlov A.R. *Phys. Rev. E*, 2003, 67, 051901

My Institute at the University of Ulm changed name starting from 2012: instead of Polymer Science Institute it is now called Institute of Advanced Energy-Related Nanomaterials

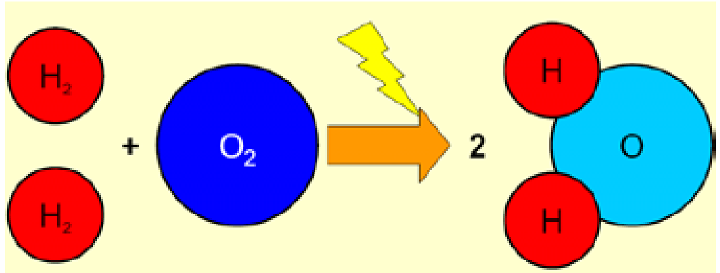
Fuel Cell: Principle Scheme



$$H_2 \rightarrow 2H^+ + 2e^-$$

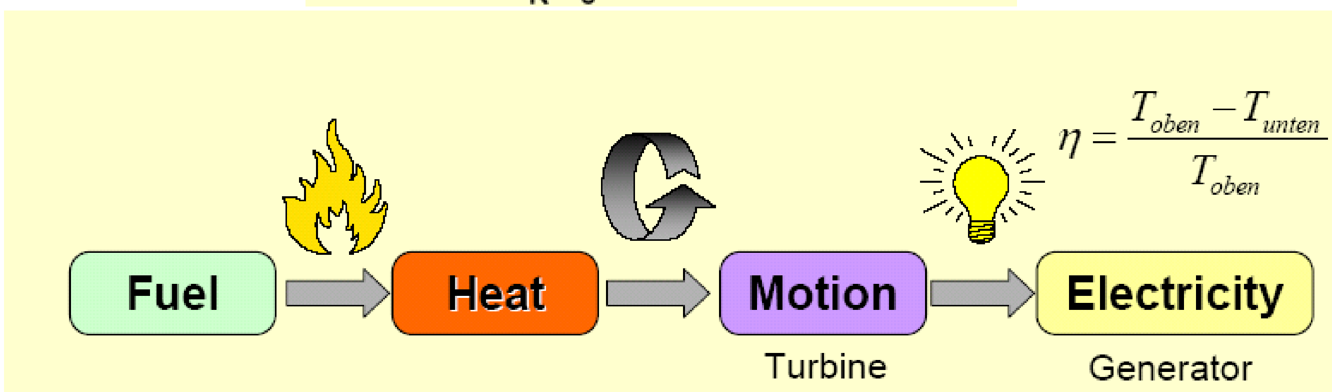
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

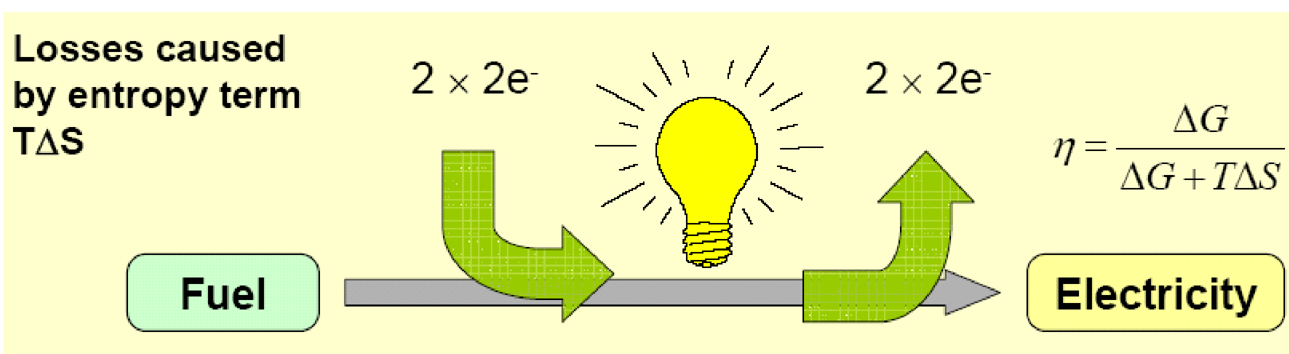
Electrochemical process and direct fuel combustion



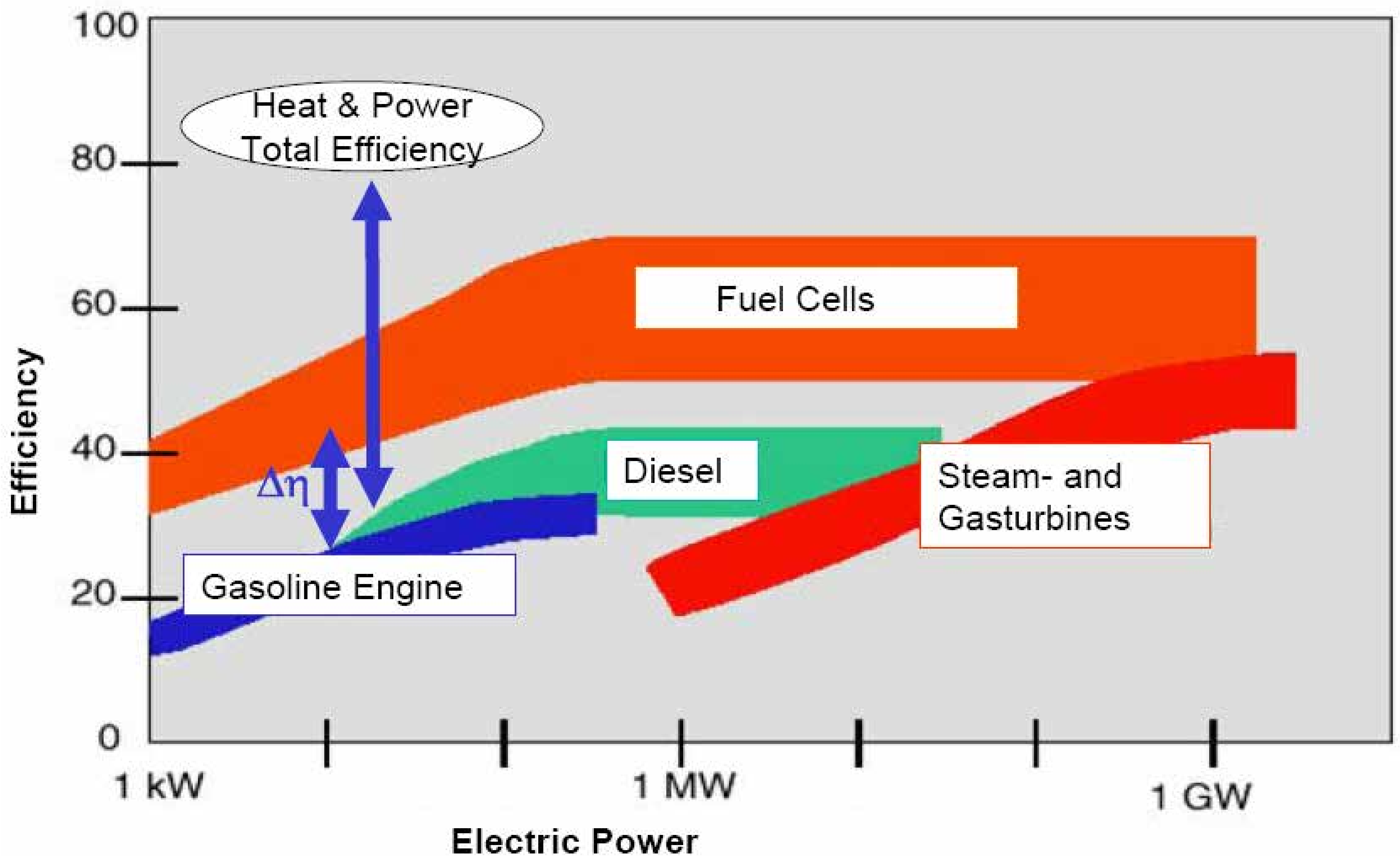
$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O\ (l)$$

$$Q = \Delta_R H_o = -286\ \mathrm{kJ/mole}$$

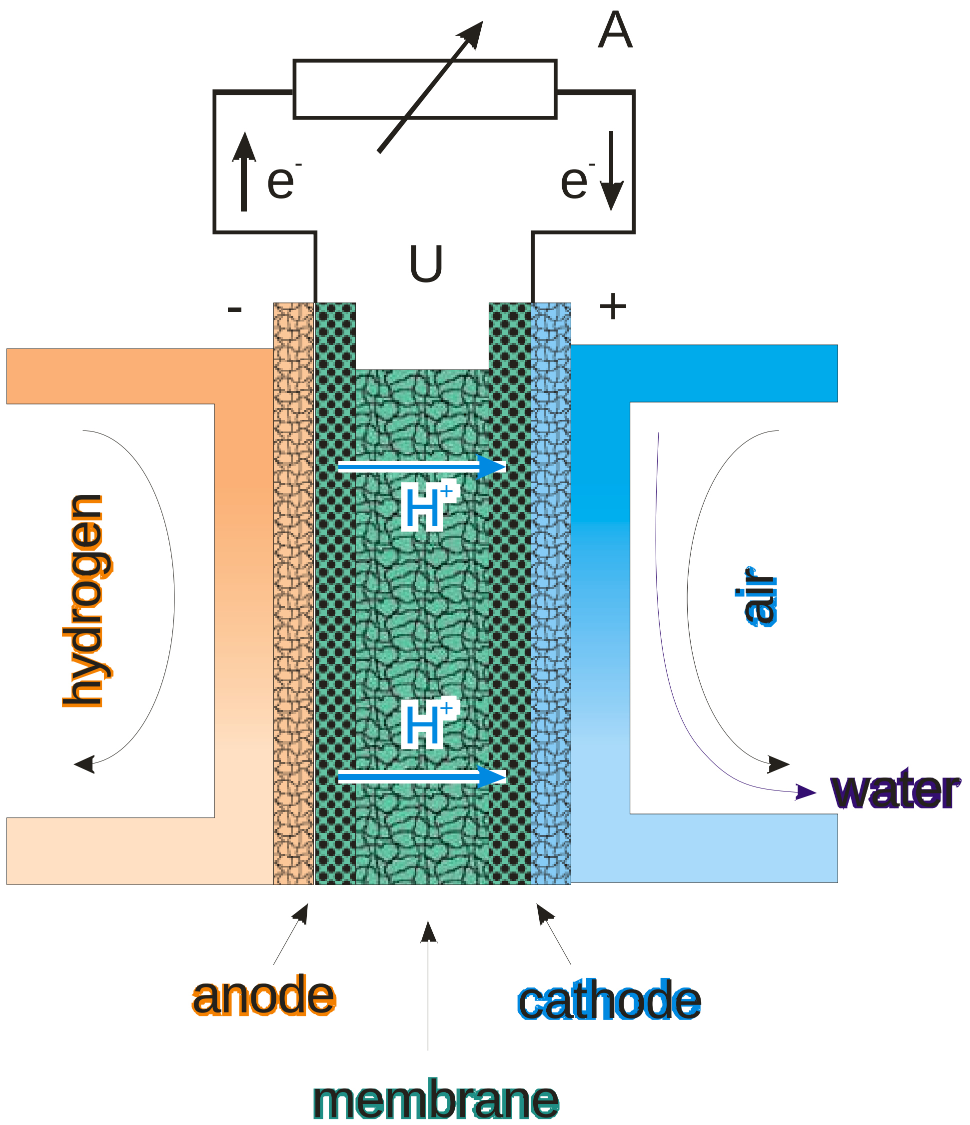




Comparison of Efficiency of Different Methods of Generation of Electric Power



General scheme of FC MEA



$H_2 \rightarrow 2H^+ + 2e^-$ $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

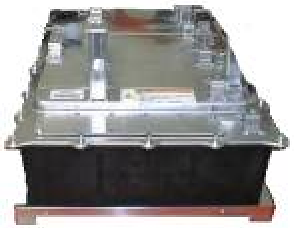
EMF of the element is determined by the free energy changing in the chemical reaction (1.23 V at 20° C for H_2/O_2).

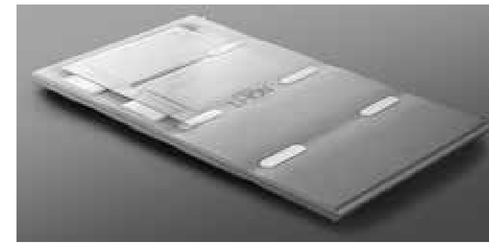
Polymers in FC: both in membrane and in electrodes

Possible applications of polymeric FC

- Transport / vehicle applications
- Stationary / reserve power systems
- Portable application

Modern car working from fuel cells: NISSAN X-TRAIL FCV

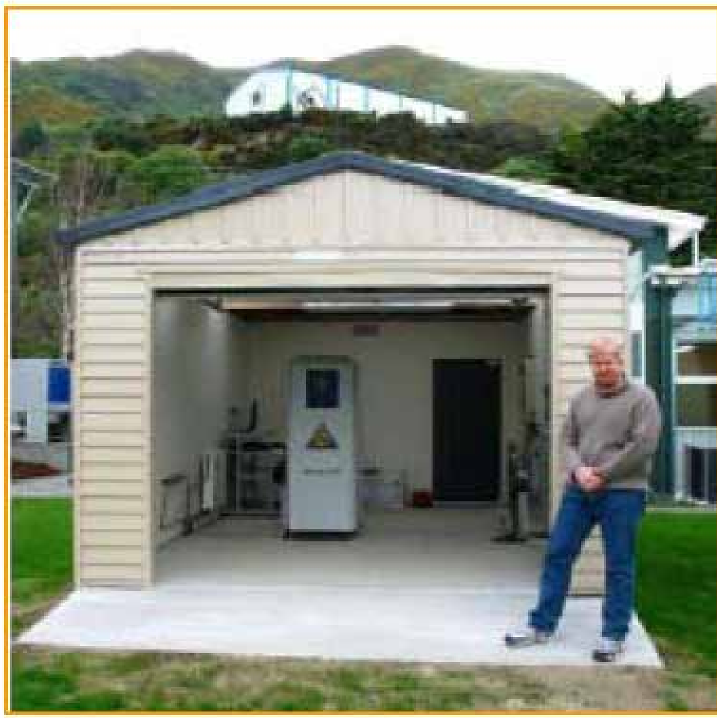




Curve Weight	1790
Seating capacity	5
Top speed (km/h)	150
Cruising range （km）	370
Max. power（kW）	90

Stationary Fuel Cells Power Stations

- Providing decentralized electricity and heat for houses
- Integrated electrochemical power stations using renewable energy sources



Portable devices

Minimum requirements for the price per kWt

but:

Maximum requirements for users convenience, infrastructure size

General requirements for polymer membrane

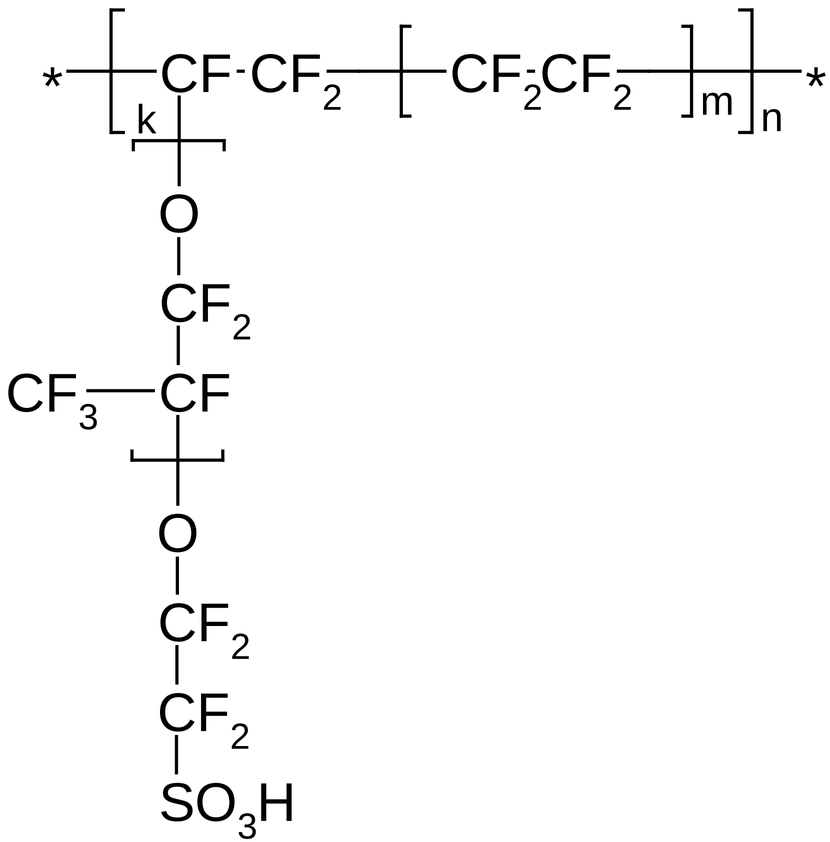
(to reduce losses and to increase lifetime)

- High proton conductivity
- Absence of electron conductivity
- Long time mechanical stability (in the presence of water)
- Low permeability for molecular reagents
- Chemical stability (hydrogen peroxide, peroxide radicals, water, acidic conditions)

Main types of polymeric FC

- Temperature regime of operation:
  - up to 80 °C, Nafion-type polymer membranes, extra pure hydrogen fuel is required (with Pt-catalyst)
  - up to 120 °C (target), composite and/or hydrocarbon based polymer membranes, less expensive fuel is acceptable
  - 130 – 180 °C, PBI-based polymer matrices for phosphoric acid electrolyte, reformate – hydrogen with 1-3% of CO is acceptable

Perfluorinated polymer sulfonic acids (Nafion etc.)



- mainly:
- m ~ 6.5
- 100 < n < 1000

- Nafion 117 means:
  - Equivalent weight, EW 1100 g/mol (indicates amount of sulfo-groups)
  - Thickness 0.007 inch

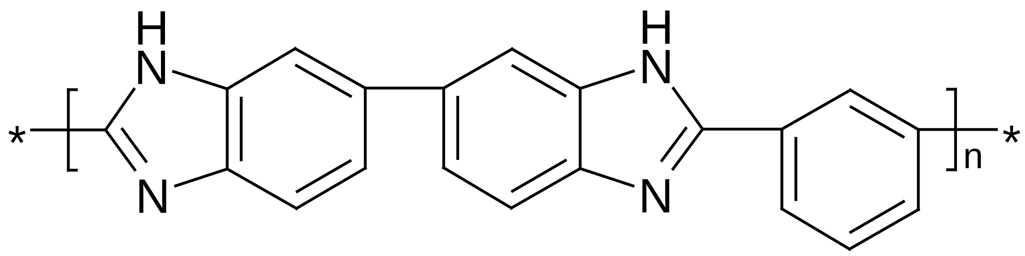
Perfluorinated polymer sulfonic acids (Nafion etc.)

- Mechanically stable and sufficiently gas impermeable at EW 1000-1100 g/mol, and thickness down to 25 mm
- (Electro)chemically stable and inert
- High proton conductivity – about 0.1 Sm/cm, (but sensitive to water presence – operational only up to 80 °C)
- High cost of production
- High crossover of methanol (bad for DMFC)
- For FC commercialization durability of thin membranes with low EW is to be improved

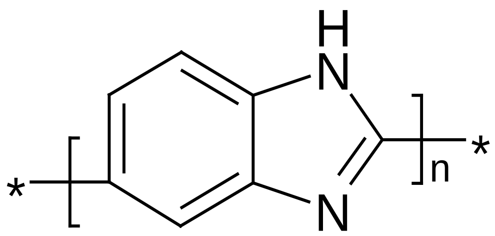
Phosphoric acid FC with polymer matrix

- Electrolyte – phosphoric acid (H_3PO_4)
- Matrix – poly(benzimidazoles) or some other heterocyclic nitrogen-containing base polymers
- Operation temperature ~ 130–180 °C (more simple heat utilization)
- Requirements on fuel purity is reduced (content of CO and CO_2), cheap fuel
- Electrodes: expensive platinum with high loading (slow oxygen reaction)
- Stability of all FC materials against corrosion in the presence of hot phosphoric acid is an issue

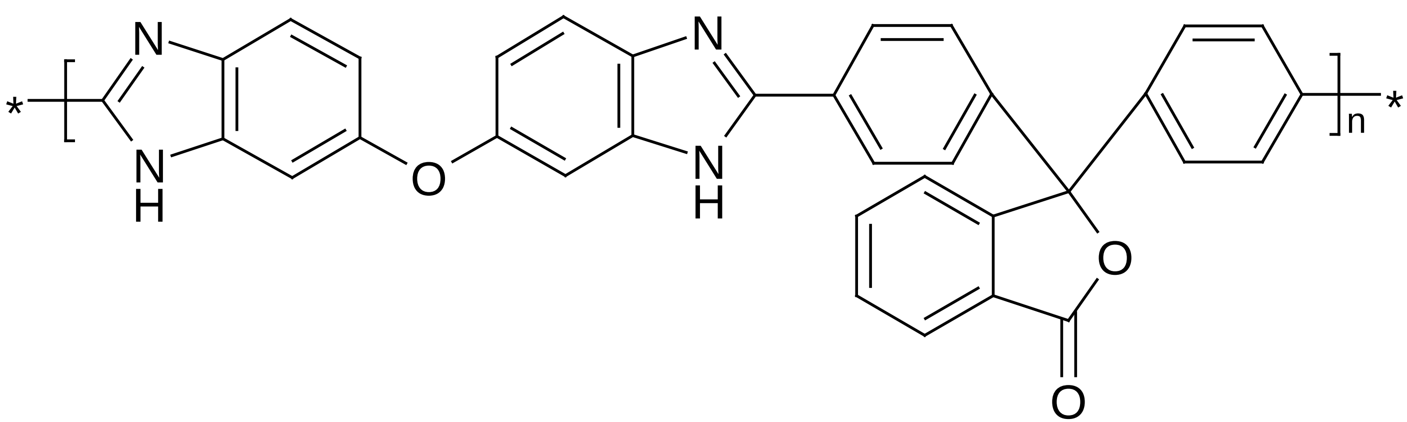
Poly(benzimidasoles)



Celazole
(BASF /
PEMEAS)



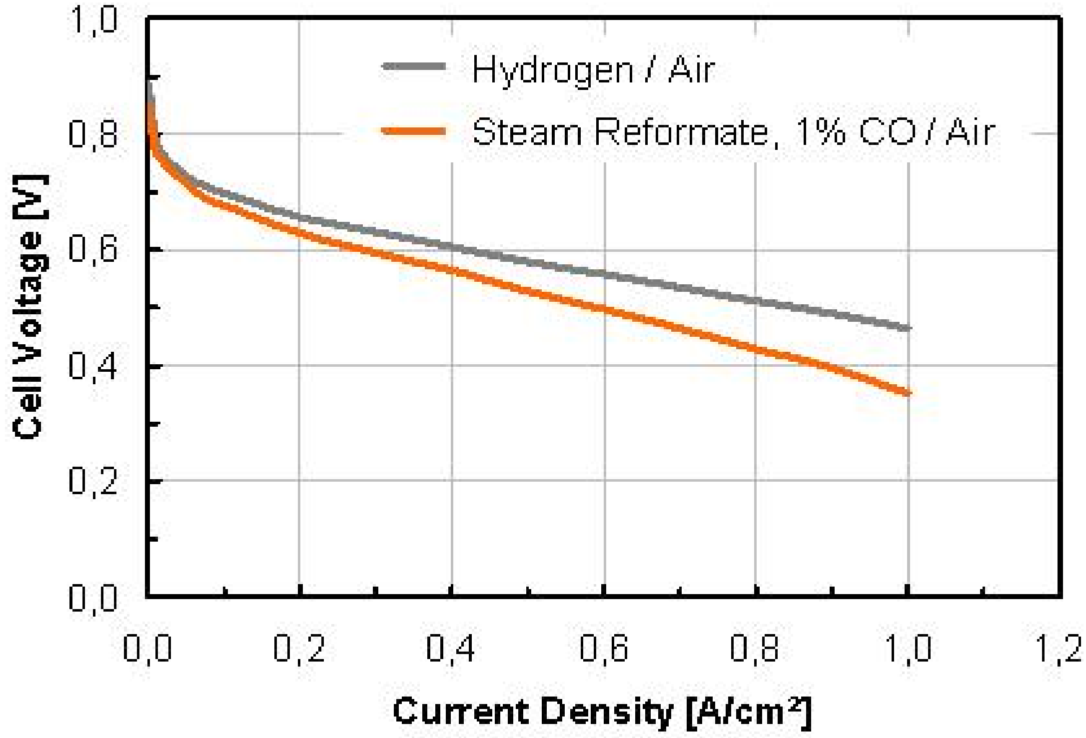
ABPBI



PBI-O-PhT
(NIC NEP)

Performance of Celtec®-P 1000 under reformate conditions

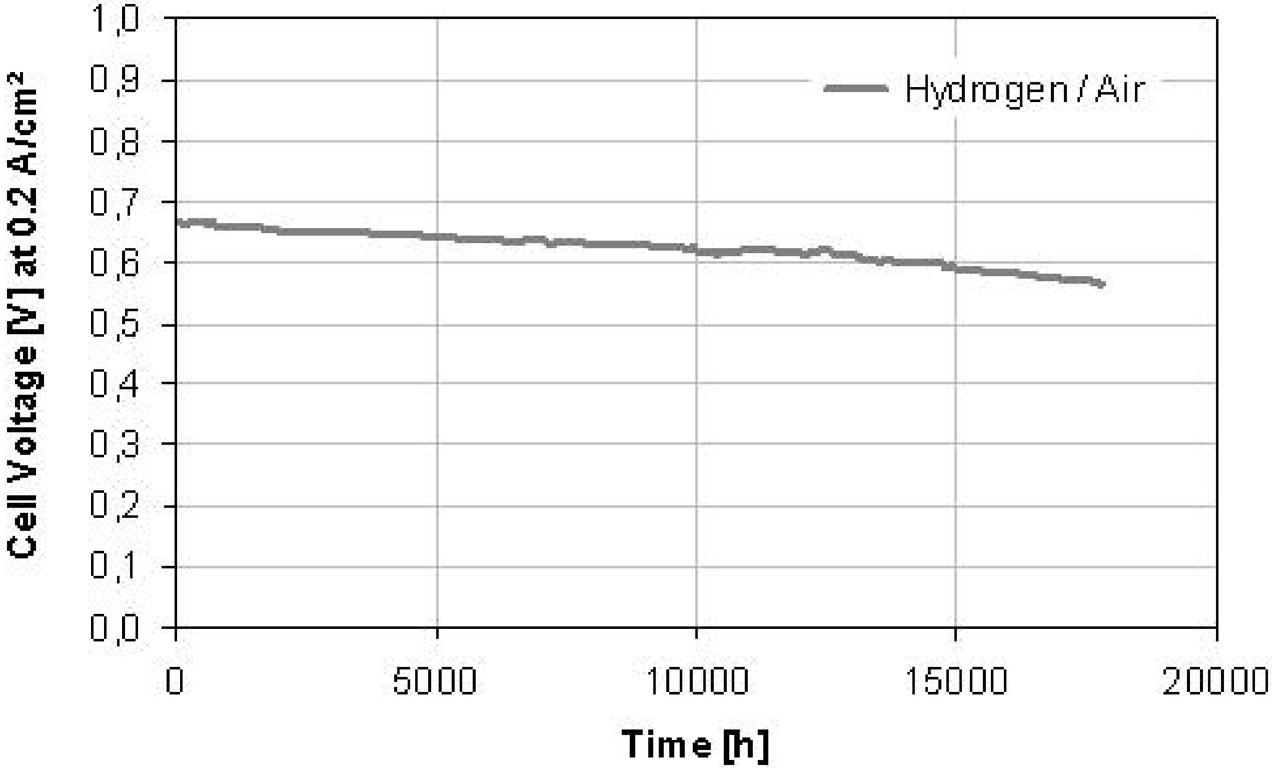
PEMEAS
Fuel Cell Technologies



Active area: 50 cm²
Temperature: 160°C
Ambient pressure
Anode: lambda 1.2
Cathode: lambda 2.0
Reformate: 70% H_2, 29% CO_2, 1%CO

PEMEAS
Fuel Cell Technologies

Durability test data of Celtec®-P 1000: More than 18.000 hours operation time

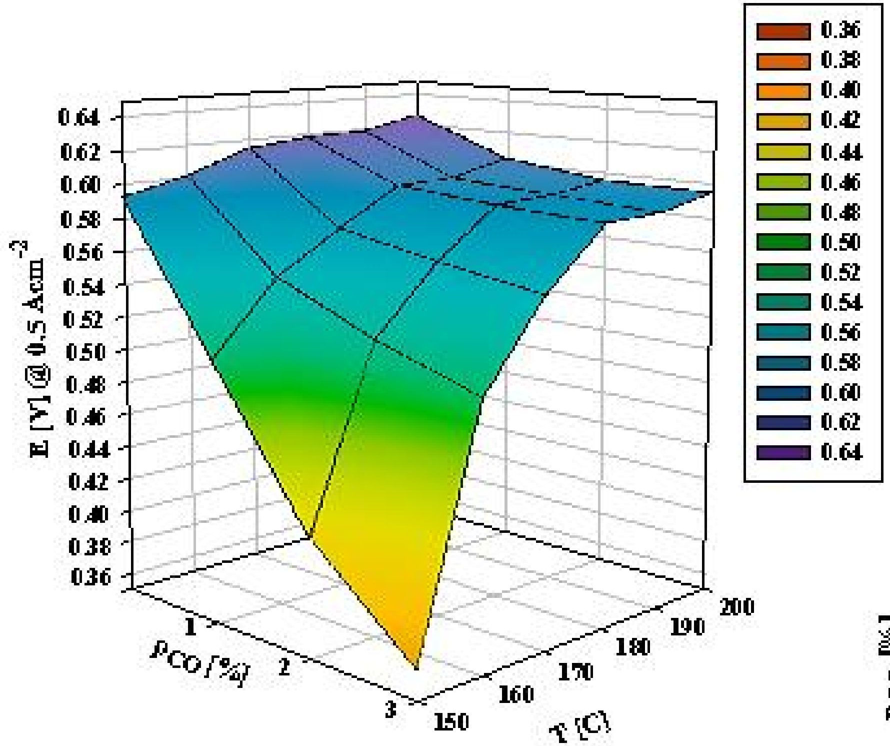


Active area: 45 cm²
Temperature: 160°C
No humidification
Ambient pressure
Anode: H_2, lambda 1.2
Cathode: air, lambda 2.0

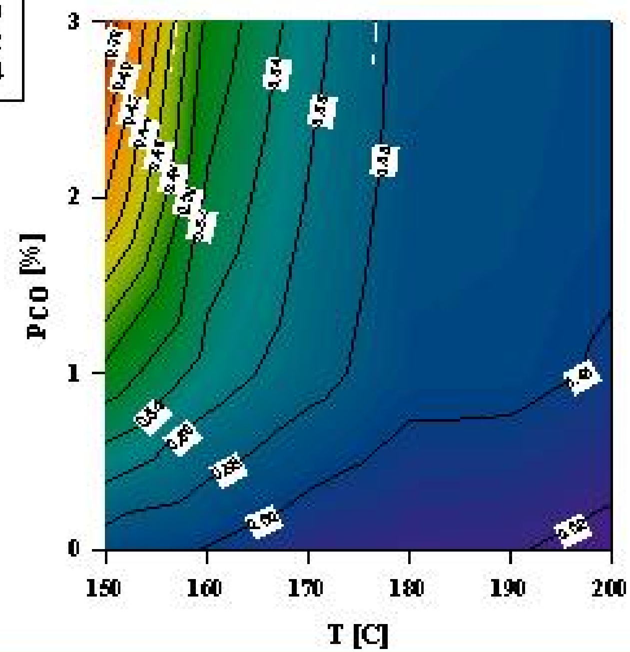
Stable long term performance with voltage drop of less than 6 µV/h

PEMEAS
Fuel Cell Technologies

CO-Tolerance of Celtec®-P Series 1000 MEA



Between 160 and 180 °C, the MEA can tolerate CO concentrations of 1 to 3 Percent



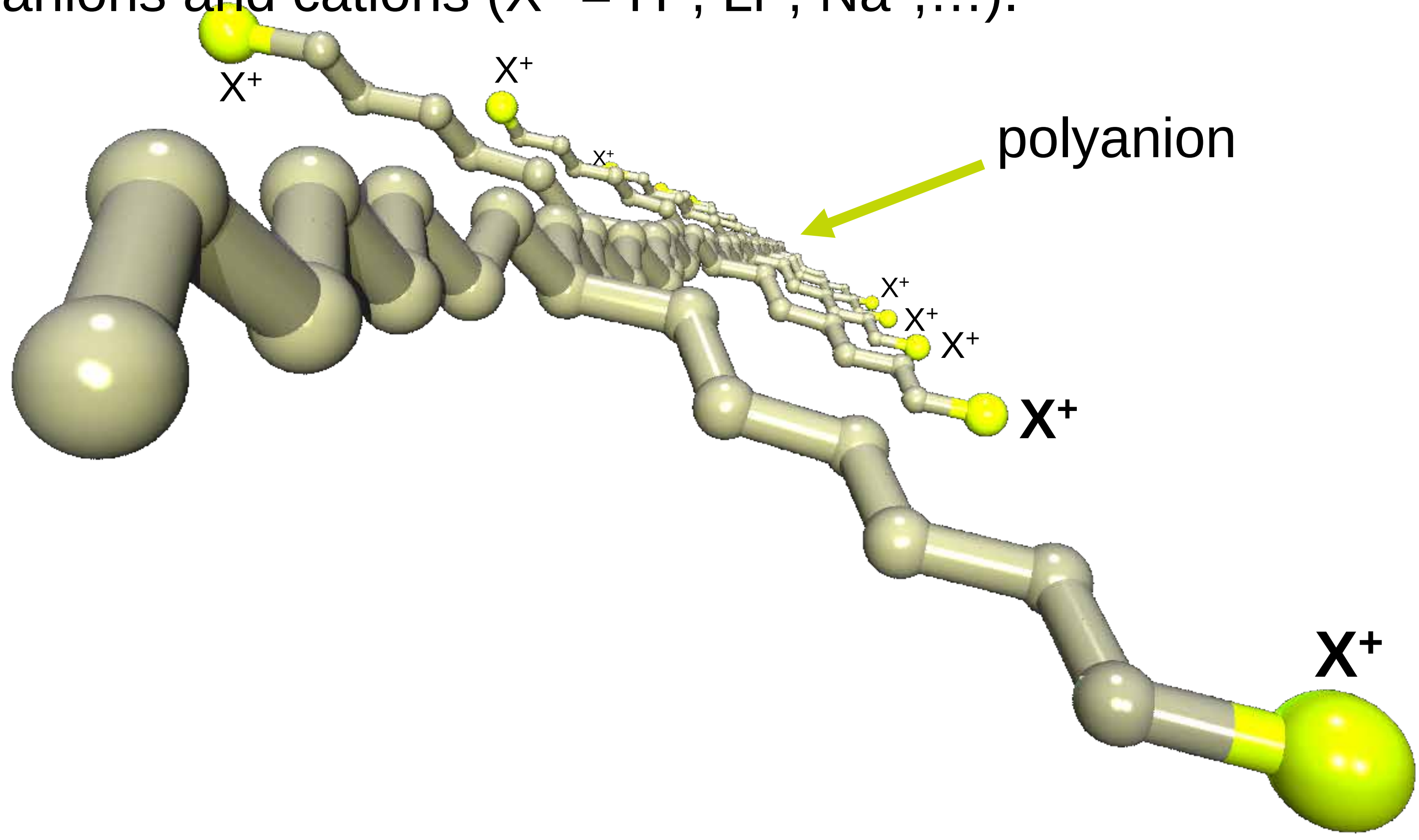
Objectives for Computer Simulation of Nafion Membrane

Using MD simulation techniques, we performed a molecular level modeling of an atomistic model of solvated polymer ionomer membrane (PIM), with the following main objectives:

- to study the basic features of specific structural organization of the system
- to elucidate details of the ionic transport though the hydrophilic regions of the membrane

Macromolecule of Nafion

In the presence of a polar solvent (water, methanol), the SO_3H groups are partially dissociated to form solvated SO_3^- anions and cations ($X^+ = H^+$, Li^+, Na^+,…).



Interaction parameters

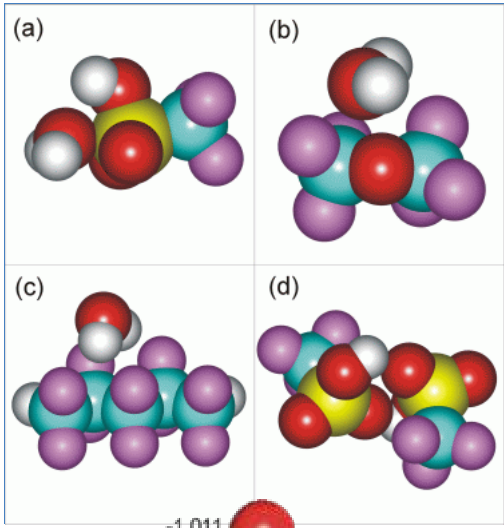
We perform semi-empirical and *ab initio* quantum mechanical calculations (CNDO, INDO, MNDO, ZINDO/1, AM1, PM3, STO-3G*, 6-31G**) on molecular structures and energies of the polymeric backbone and pendant chains of Nafion® with and without additional water (methanol) molecules. To this end, some model systems are considered, including:

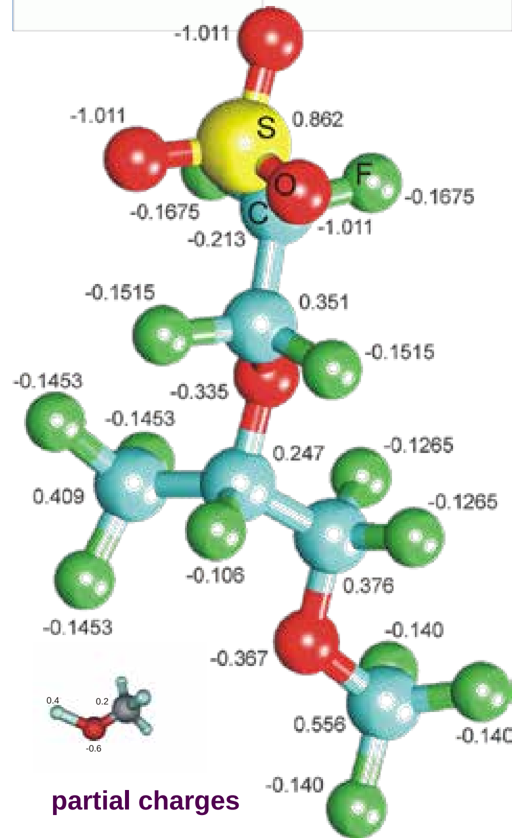
$CF_3OCF_2CF(CF_3)OCF_2CF_2SO_3H$

$CF_3CF_2CF_2CF_2CF_3$

$CF_3SO_3H + H_2O$, $CF_3OCF_3 + H_2O$,

$H(CF_2)_5H + H_2O$

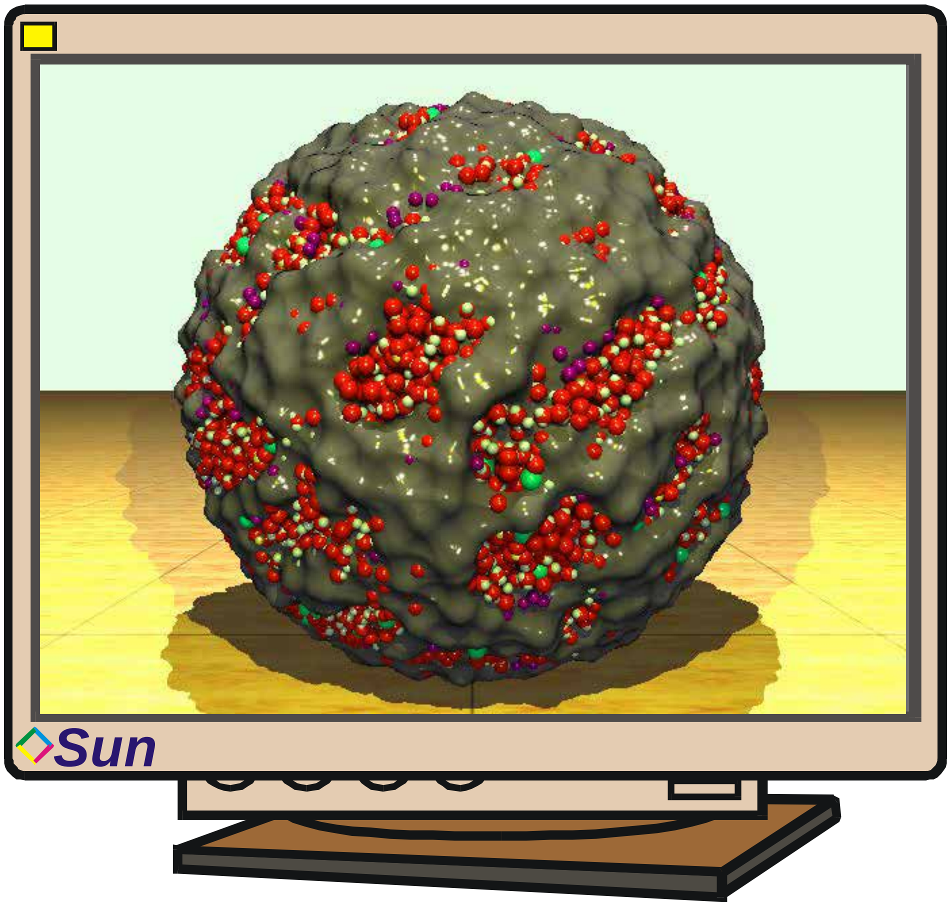


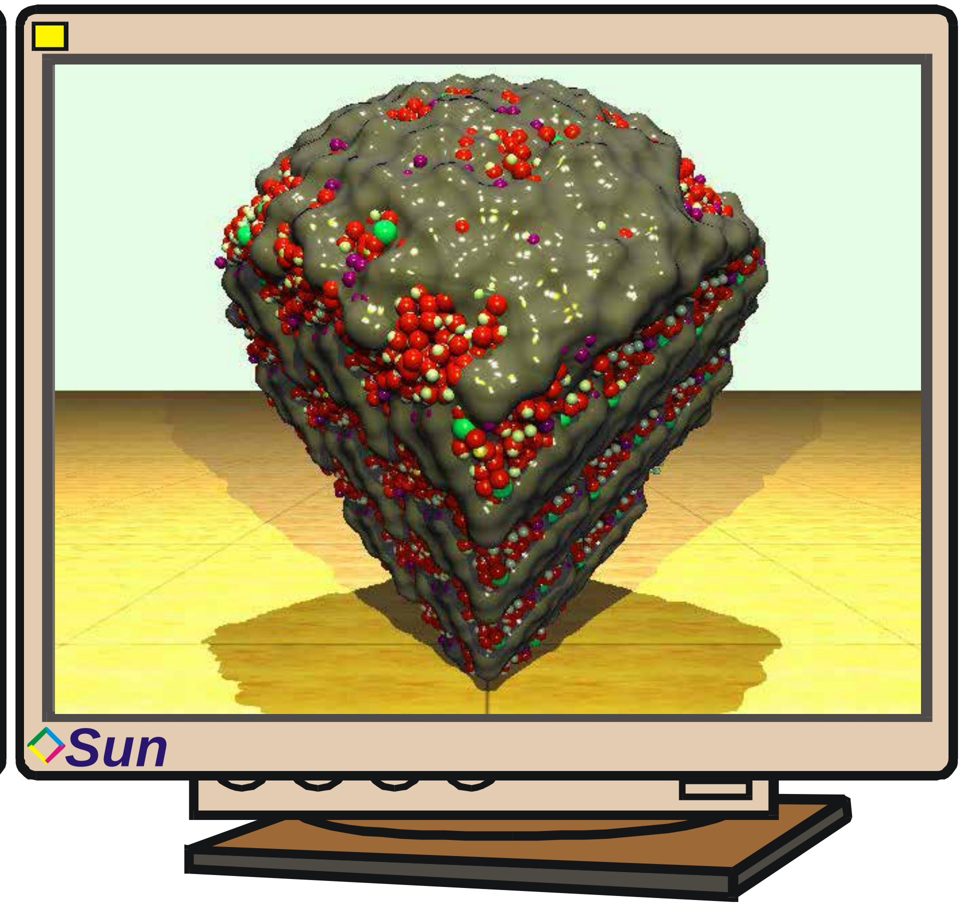


partial charges

Morphology

(Connolly surface for hydrophobic atoms)

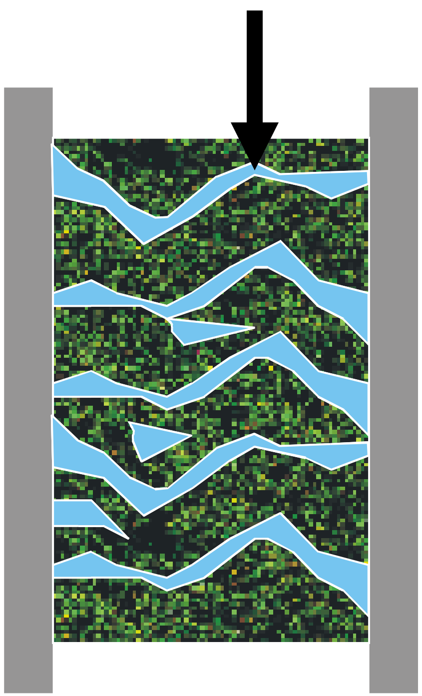




Nanoscale segregation

<u>Microphase separated system</u>:

water clustering around SO_3 groups
hydrophobic/hydrophilic regions
hydrophilic clusters (size » 35 Å)
water channels (d » 10 Å) ®
ion conduction pathways



Connolly surface for hydrophobic atoms (we "remove" polar component)
"the piece of coke or foam"

Fuel cells: commercialization into Russian markets

Joint Stock Company National Innovation Company "New Energy Projects" was established in 2005 in order to implement R&D projects in the field of hydrogen-based energy and to commercialize those projects in Russia.

Main investor: Norilsk Nickel Industrial Complex (NNK) - world leader in Nickel and Palladium production, one of the largest producer of Platinum and Copper

Russian partners:

- Russian Academy of Science
- Moscow State University

International cooperation:

- Fumatech
- Nedstack

Applications of fuel cells to Russian market

Backup Power Supply

Telecommunication towers, critical backup (hospitals, police)

Russia has huge territory and developed power grid, the density of telecom towers is the same as in smaller countries.

Backup units based on Low temperature fuel cells (3-30 kW range, 5000 hours of operation run on pure H_2)

- longer runtime
- ecological purity
- could be combined with electrolyzer

Applications of fuel cells to Russian market

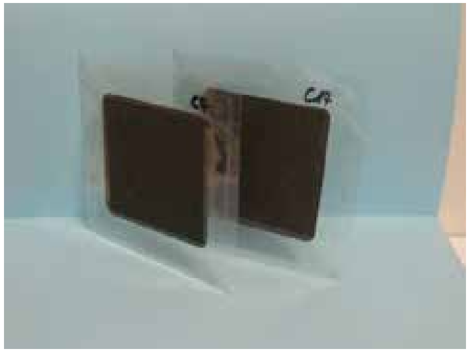
Backup Power Supply :

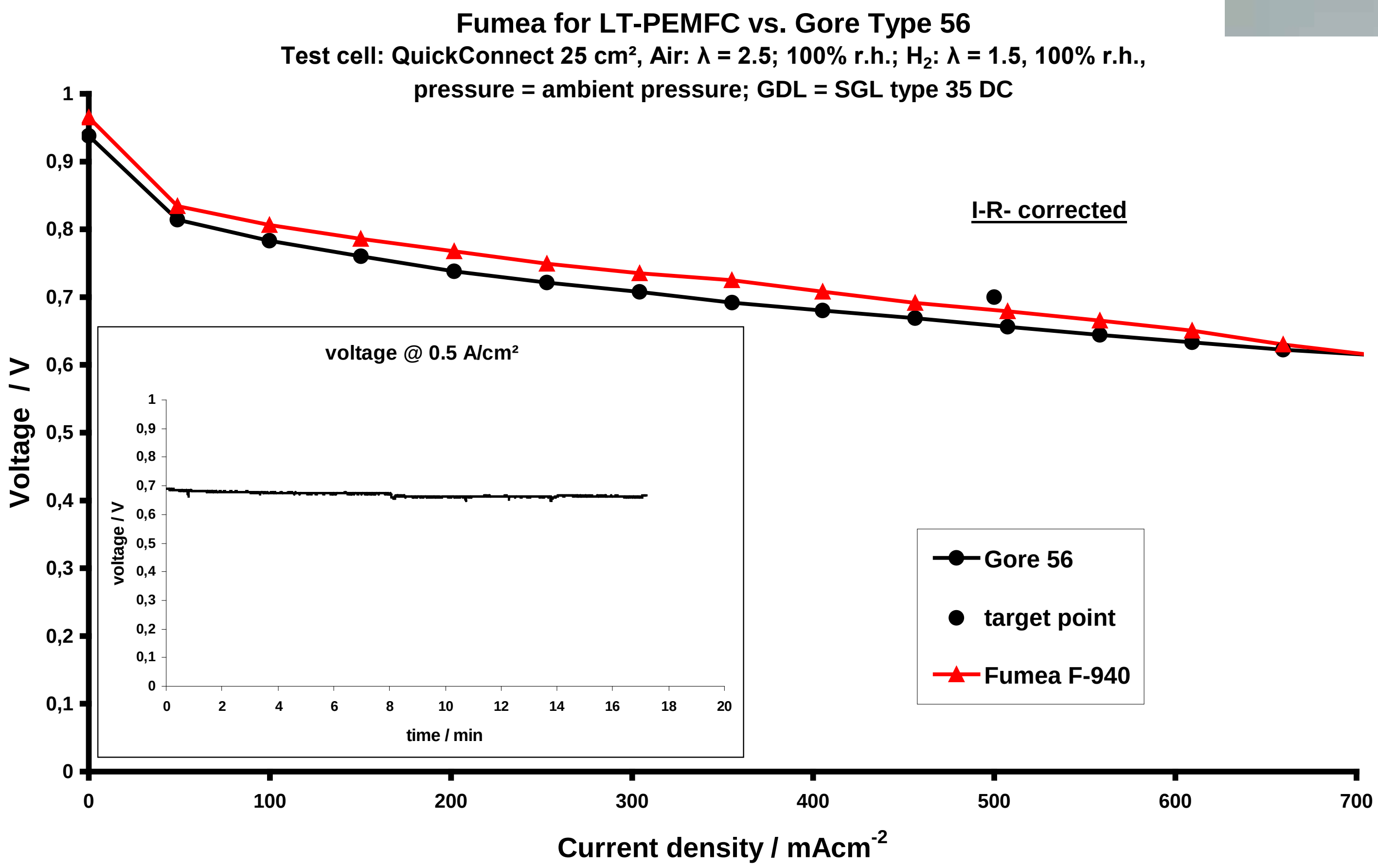
development of low-temperature membrane-electrode assemblies

Based on PFSA (analogous of Nafion® membrane) membrane developed by Fumatech

- Operation temperature 65C
- Characteristics not worse than world leaders: 3M, Gore
- Price at least 3 times less (300USD/1kW)

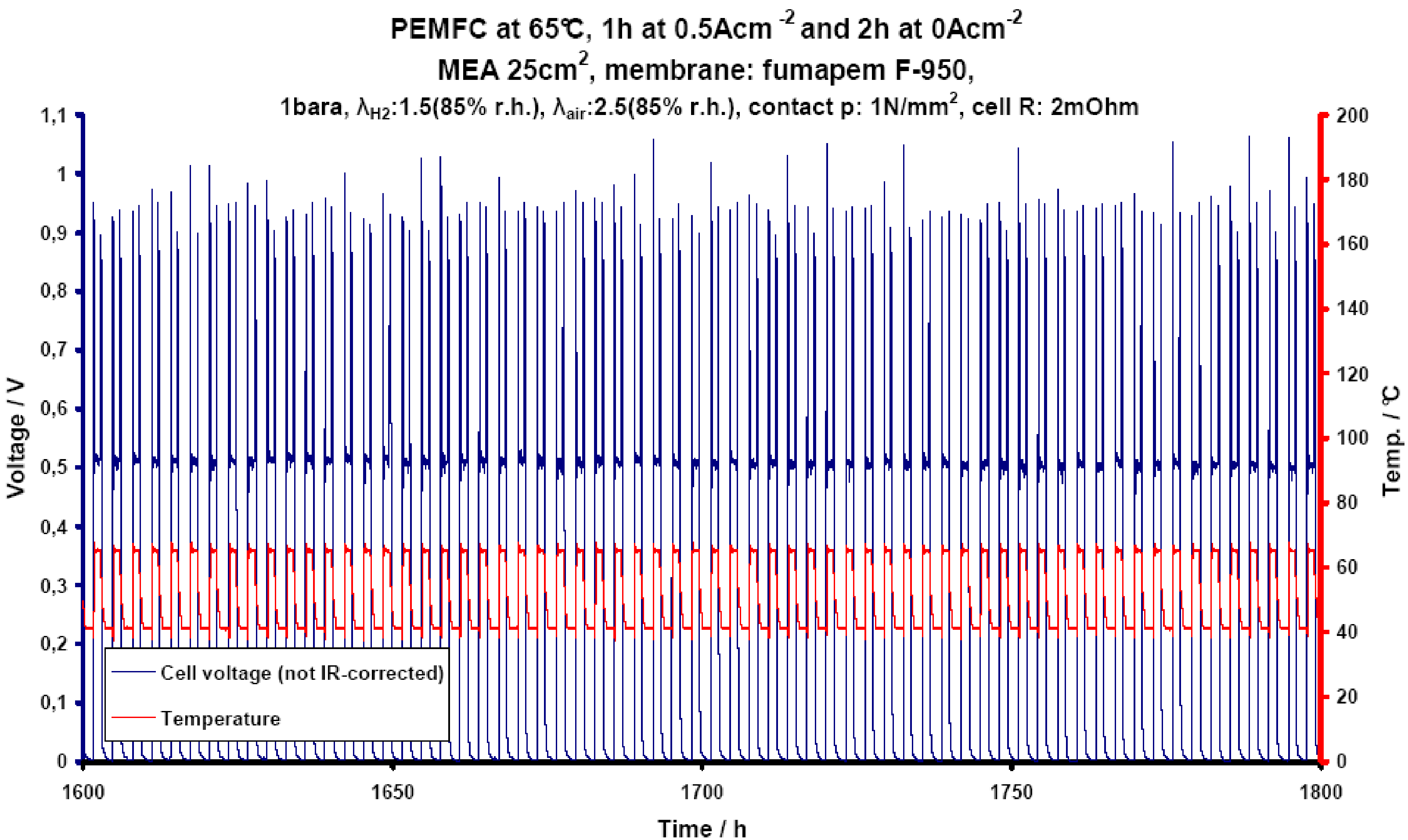
Development of low-temperature membrane-electrode assembly





Same performance as Nafion® membrane.

Development of low-temperature membrane-electrode assembly: durability is the main issue



Cycles loading is one of the critical regimes.

Developed MEA demonstrates excellent durability (less than 20 µV/hour)

Applications of fuel cells to Russian market

Off-grid power supply and heat cogeneration:

Distant Single houses and villages

Municipal grids of heat and electricity provision are old and not flexible, instead of total reconstruction it could be possible to create a set of independent off-grid power systems.
To supply natural gas pipeline to most places in Russia – social responsibility of Gazprom company.

Elevated temperatures fuel cells:

- •Electricity and heat cogeneration, efficiency up to 85%
- •CO tolerance up to 3% - natural gas after shift reformer cold be used
- •No noise and exhaust – could be installed inside the building

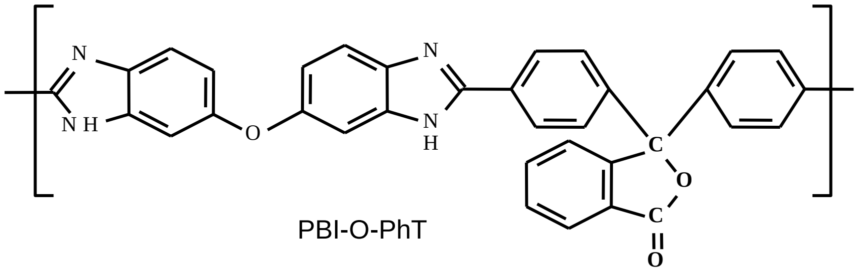
Applications of fuel cells to Russian market

Off-grid power supply and heat cogeneration:

Development of PBI-based membrane electrode assemble

New patented formulae:

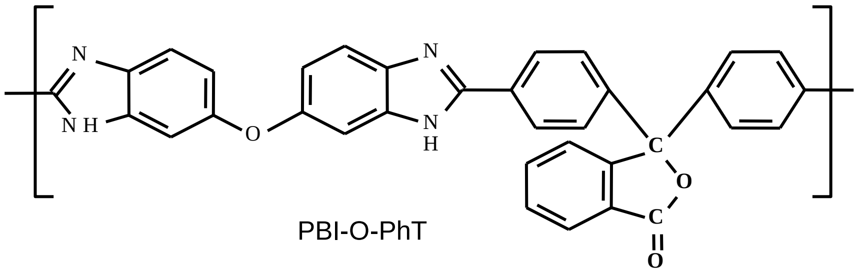
Crosslinked PBI-O-PhT



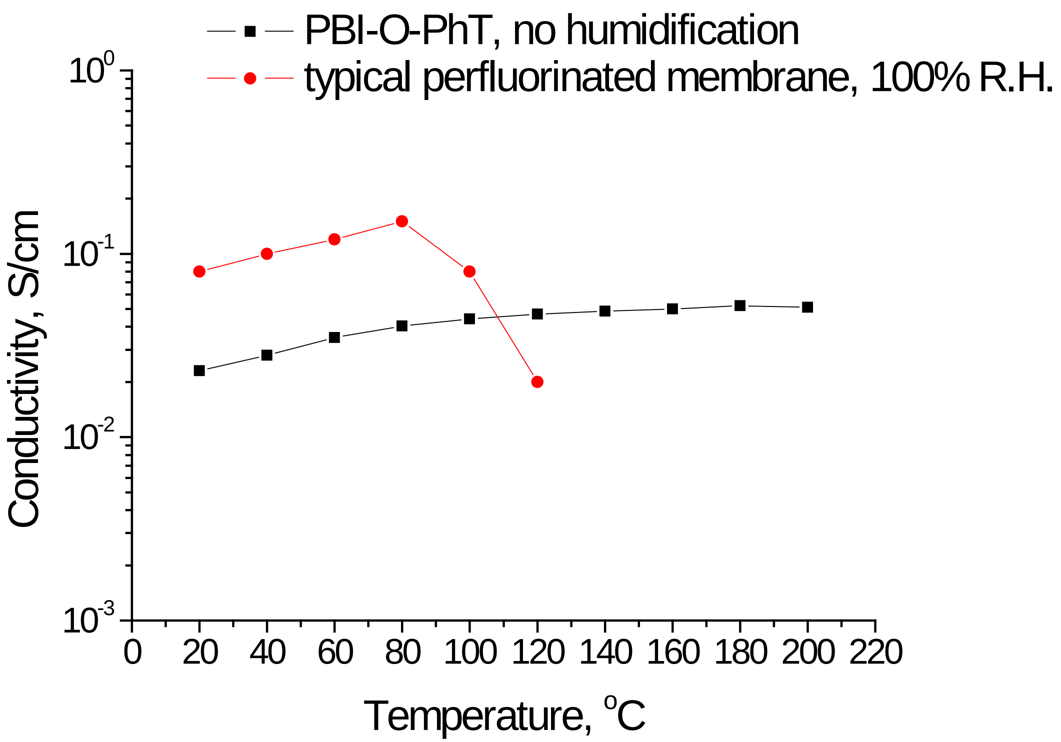
PBI-O-PhT

- better processability than standard PBI Celasole®
- no carcinogen (diaminobenzidine)
- simple casting
- stable at polyphosphoric acid at 180C.

PBI-O-PhT membranes

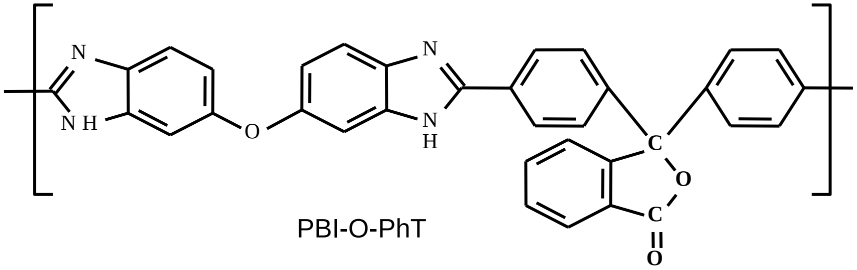


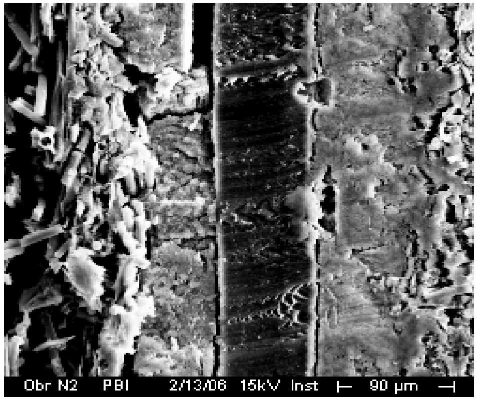
PBI-O-PhT



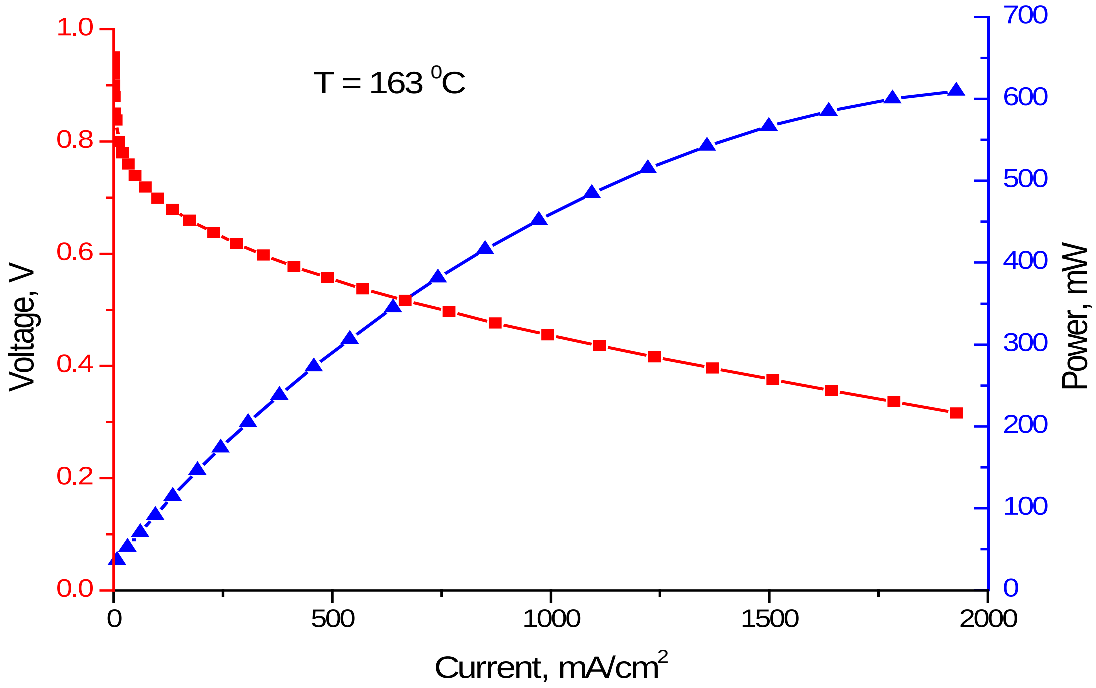
Conductivity is less than for Nafion®, but no temperature decline at high temperatures

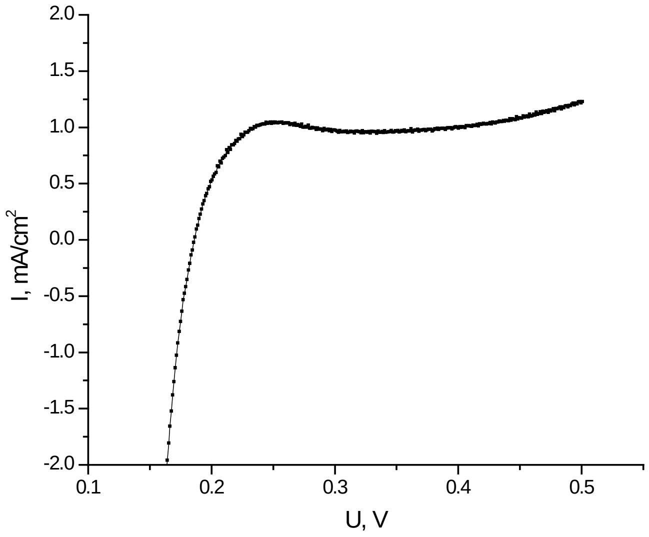
PBI-O-PhT MEAs





MEA cut-off

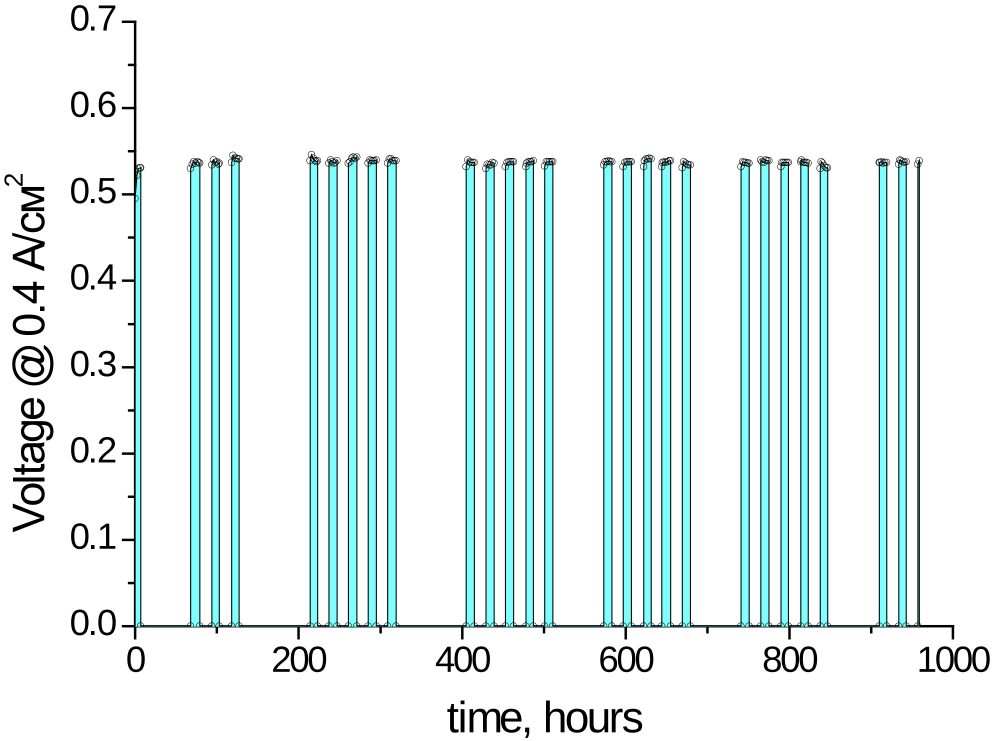


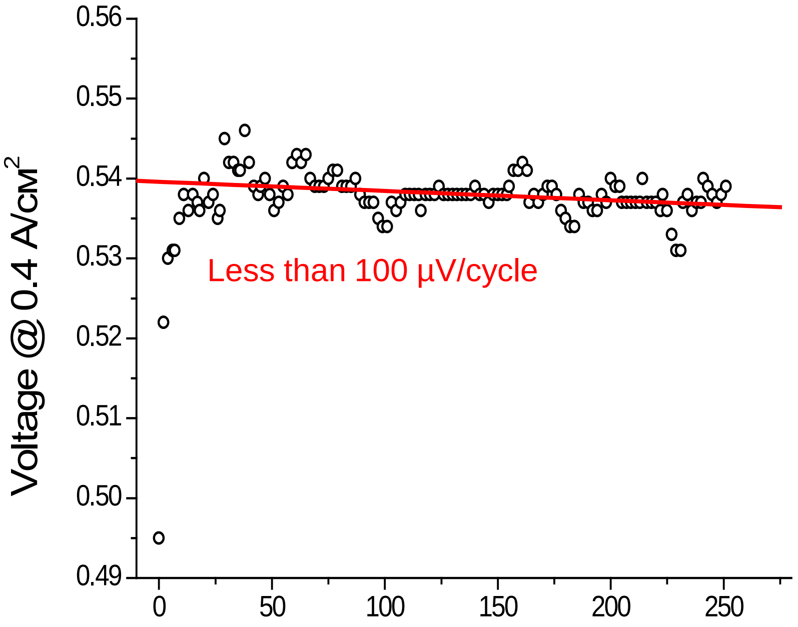


Crossover: <1mA/cm^2

Characteristics are similar to Pemeas (BASF)

PBI-O-PhT MEAs: durability





No durability during reasonable time period (target running time – 40 000 hours)

Accelerated tests: 24 hour start-stop cycles.