

# **Kann man Plasmapolymere mit klassisch-chemischer Struktur und entsprechend hochwertigen Eigenschaften erzeugen?**

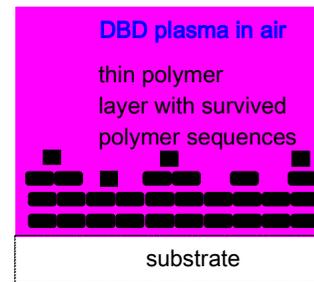
**Is it possible to produce plasma polymers with a classical chemical structure and thus with high-quality properties?**

**Jörg Florian Friedrich**

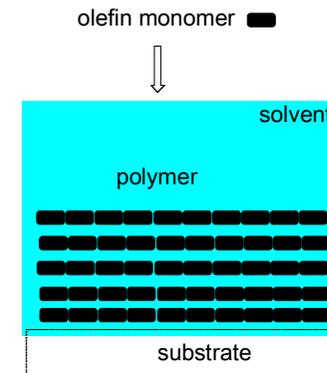
Technische Universität Berlin

# Can a classical chemical structure of a plasma polymer layer be achieved by replacing monomers with polymers ?

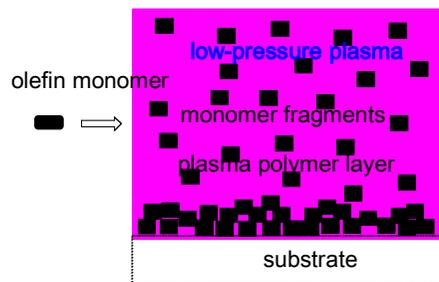
Plasma polymerization by spraying of dissolved polymers to form a polymer with a majority of intact molecular sequences



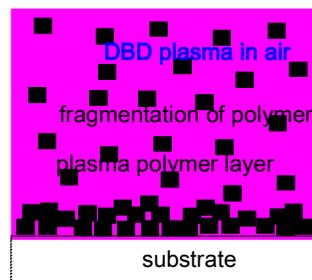
Classic chain-growth polymerization



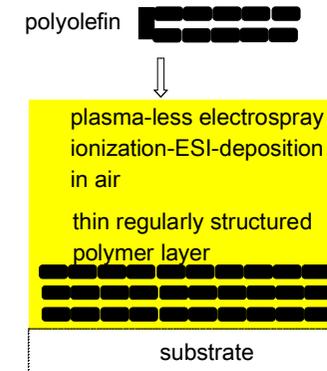
Plasma polymerization using monomers



Plasma polymerization by spraying of dissolved polymers to form a polymer with a complete irregular structure

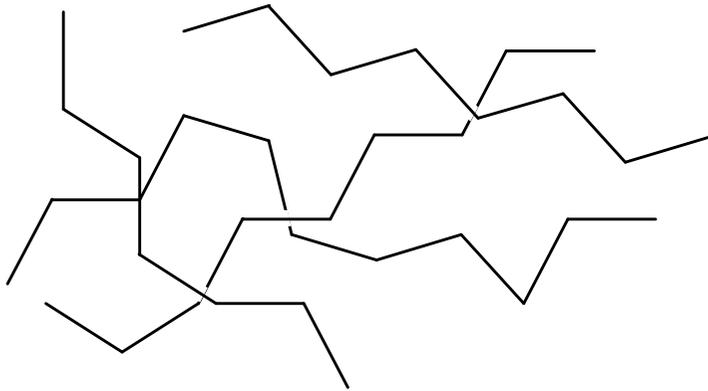


Polymer deposition using polymer spray

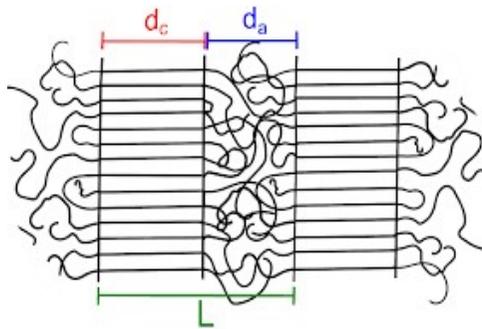
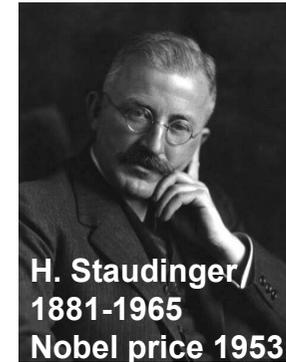


# Classic polymers

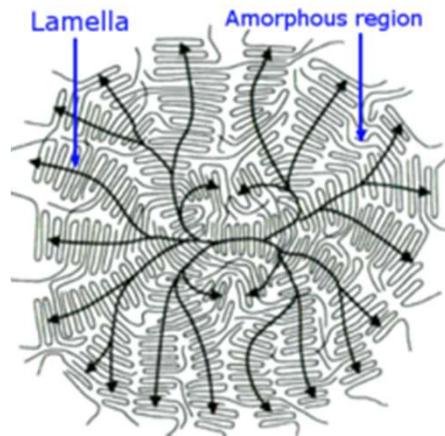
What does the classic polymer structure look like and can it also be generated during plasma polymerization and how?



German organic chemist who demonstrated the existence of macromolecules, which he characterized as polymers (1920).



lamellae



spherulite

Today's ideas on polymer structure based on Kanig's studies [G. Kanig, H. Bauer, H. G. Kilian, H. G. Zachmann, R. Hosemann, Kristallisier- und Schmelzvorgänge bei Polymeren, Coll. Polym. Sci. 260, :356-377 (1982)]

# Classic chain-growth polymerization

Can the plasma start a classic chain-growth polymerization?



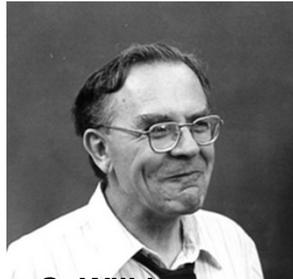
**K. Ziegler**  
1898-1973  
Nobel price 1963



**G. Natta**  
1903-1979  
Nobel price 1963



**E. O. Fischer**  
1918-2007  
Nobel price 1973



**G. Wilkinson**  
1921-1996  
Nobel price 1973

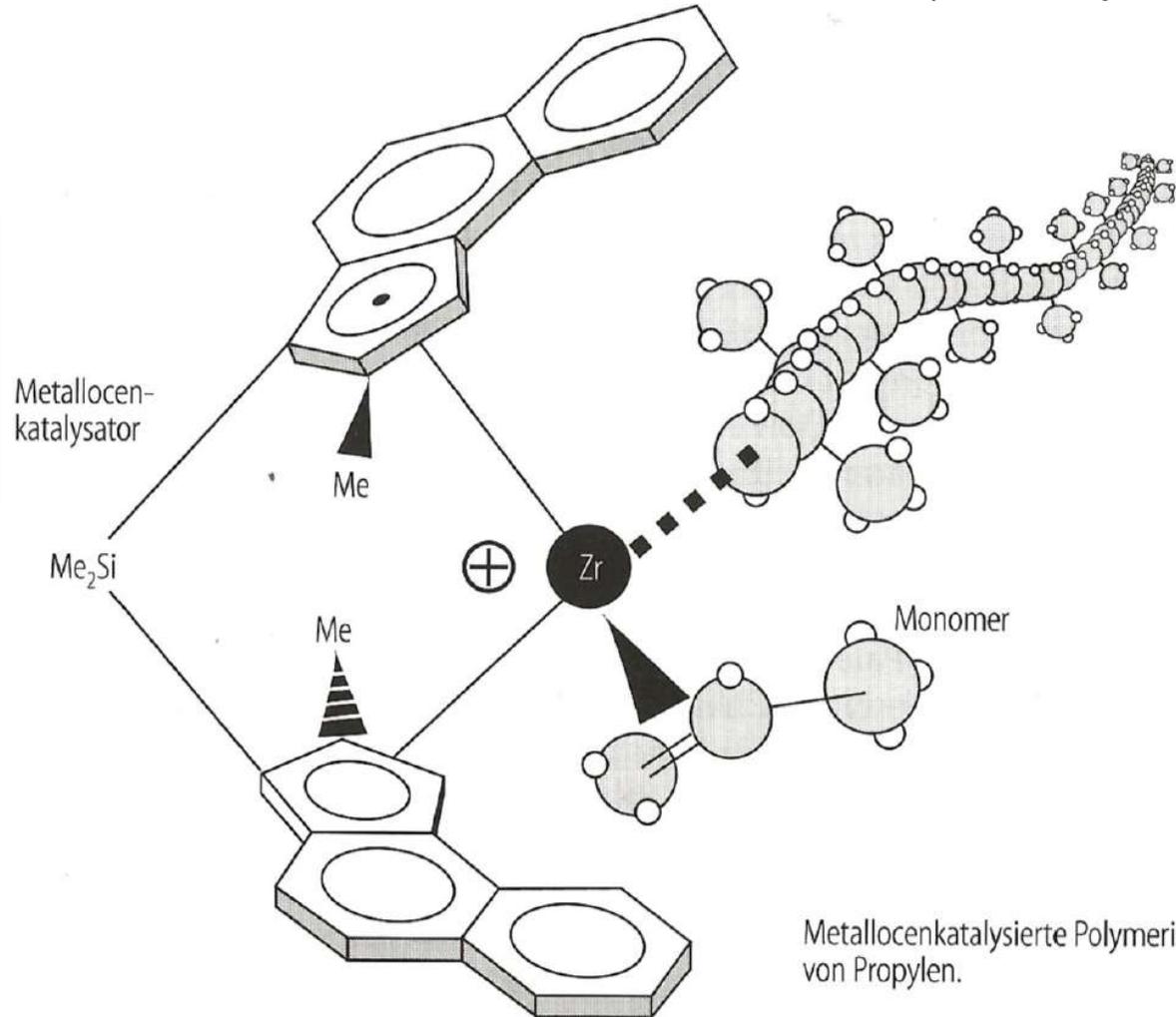


**W. Kaminsky**  
1941-

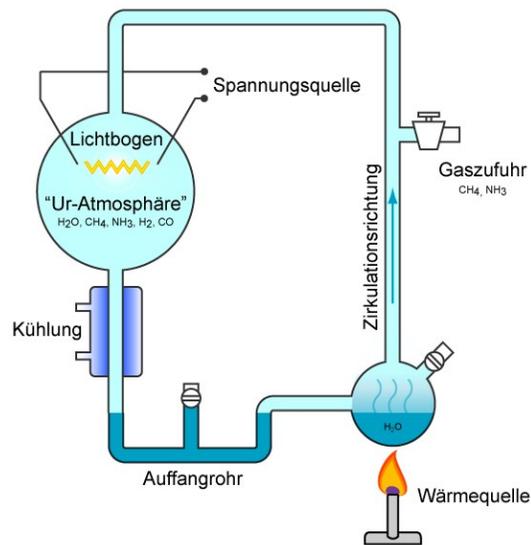


**H. Sinn**  
1929-

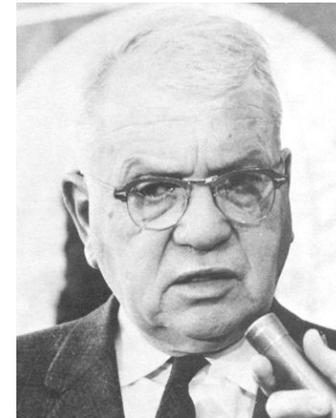
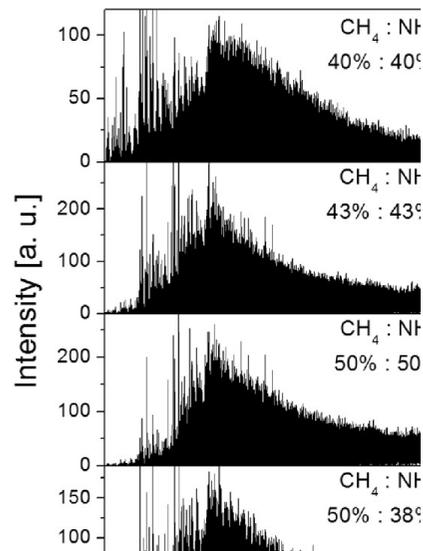
Classic chain-growth polymerization using metallocene (zircon) catalysts and MAO (methylalumoxane) co-catalysts leads to linear macromolecules (Kaminsky, Sinn)



# Pioneering atmospheric plasma synthesis of biomolecules and biopolymers in 1953



Synthesis of amino acids and nuclein bases as well as **bio polymers** using plasma in the atmosphere of the early, prebiotic Earth with  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2$



**H. C. Urey**  
1893-1981  
Nobel price 1934



**S. L. Miller**  
1930-2007

# Comparison of the structures of classic polymers with those of plasma polymers

linear chains ↔ cross-linked network with entrapped low-molecular compounds



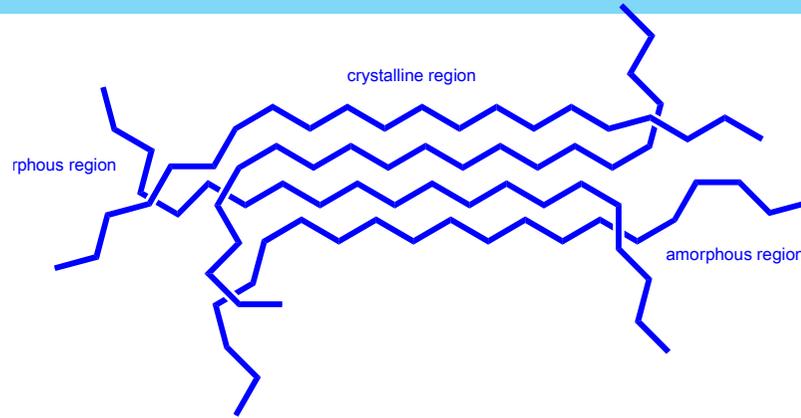
**H. F. Mark**  
1895-1992



**P. W. Flory**  
1910-1985  
Nobel price  
1974



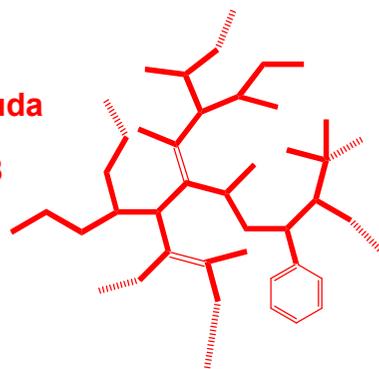
**H. K. Yasuda**  
1930-2018



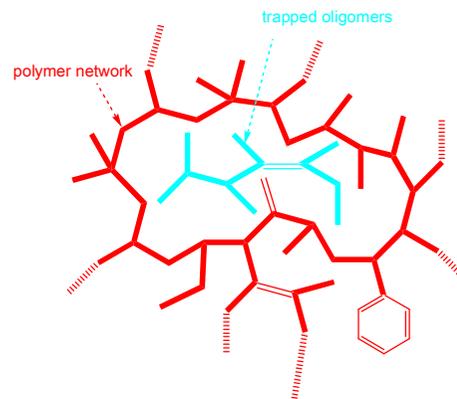
classic partially crystalline polymer

- Linear macromolecules
- Amorphous and crystalline regions
- Spherulithic or dendritic structure
- Stoichiometric composition

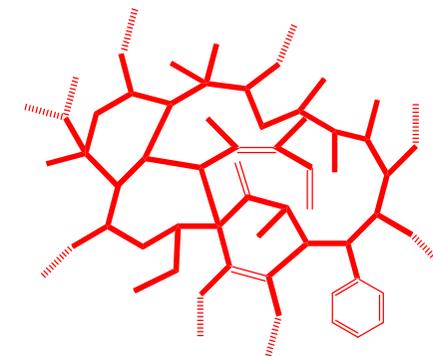
- Crosslinked network
- Low-molecular weight oligomers
- Random irregular composition
- 100% amorphous
- Irregular species, such as radicals, peroxy groups and follow-on products



Tibbitt model



advanced Tibbitt model



a-CH model

# What is the reason for the totally different structure of plasma polymers in comparison to classic polymers?

Reason is: 1) High-energy tail of the electron energy distribution and  
2) continuous energy supply through the electrical discharge

## PLASMA:

Selectivity of chemical reactions is impossible because energy excess



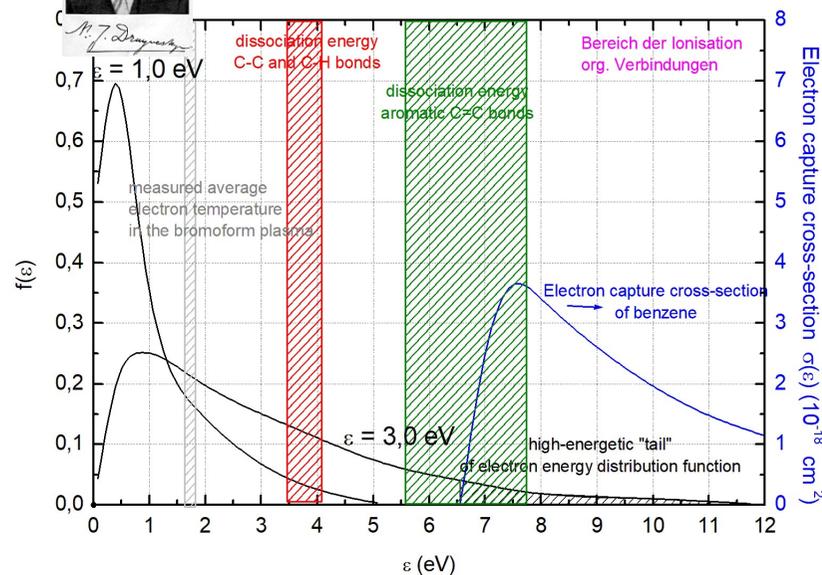
**M. J. Druyvestein**  
1901-1995



**J. C. Maxwell**  
1831-1879



**L. E. Boltzmann**  
1844-1906



- continuous (inexhaustible) supply of electrical energy
- high-energy tail of electron energy distribution
- bond dissociation energies are much smaller than the high-energy tail
- ionization energies are higher than bond dissociation energies
- permanent ion bombardment from plasma
- permanent hard UV-photon irradiation

## CHEMISTRY:

Chain-growth polymerization is a polymerization technique where unsaturated monomer molecules add onto the active site on a growing polymer chain one at a time. There are a limited number of these active sites at any moment during the polymerization which gives this method its key characteristics.

Mechanism:

1. Chain initiation
2. Chain propagation
3. Chain termination.

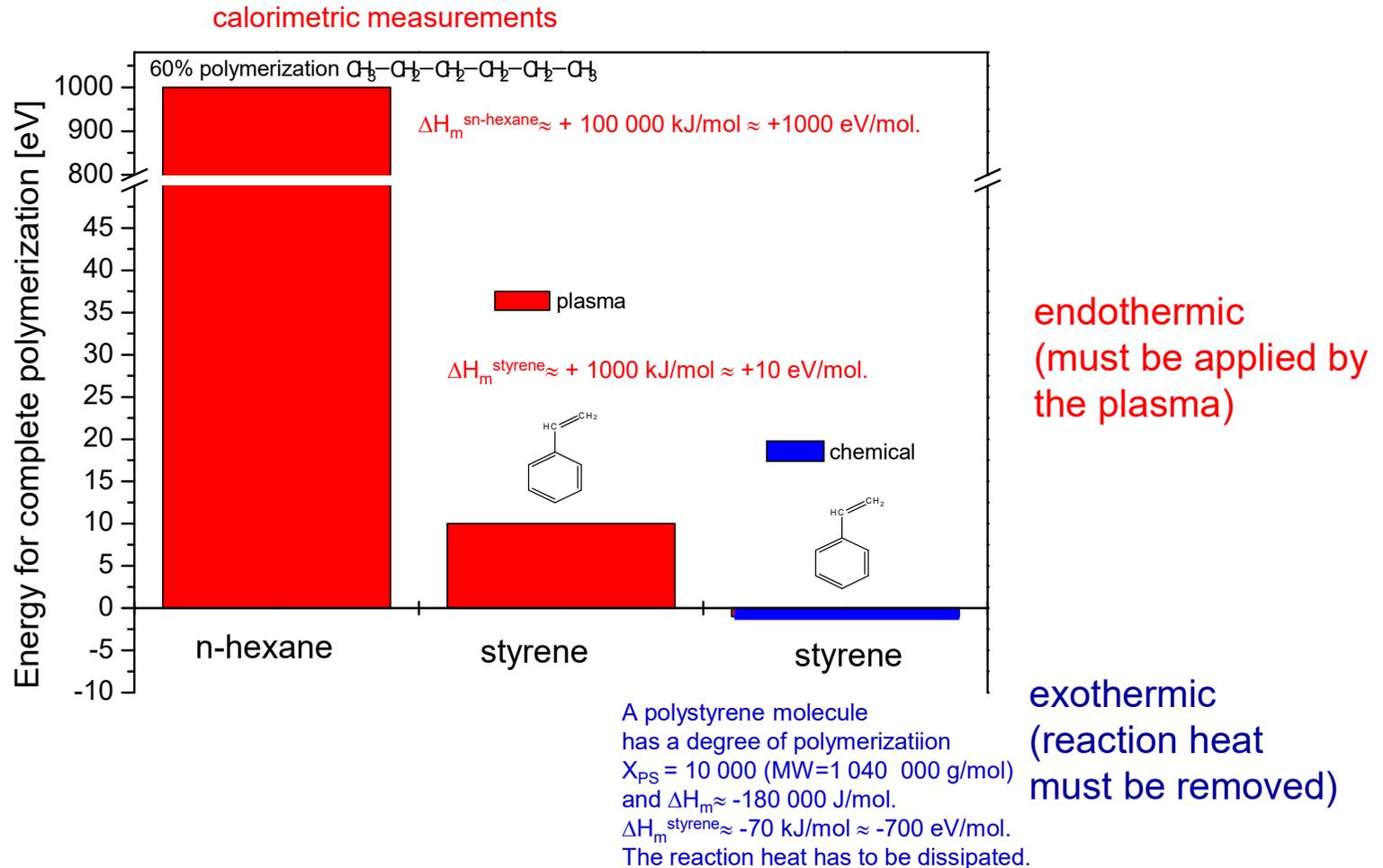
Chain polymerizations are exothermic reactions, as the resulting polymers are lower in energy than the mostly unsaturated monomers.

Styrene	-70 kJ/mol
Vinylchloride	-71
Vinylacetate	-88
Acrylonitrile	-79,4
Acrylic acid methylester	-80

With a degree of polymerization of styrene of 10,000, 700,000 kJ/mol are released per mol. In industrial processes, the considerable heat of polymerization must be dissipated by external cooling to prevent the polymerization rate from increasing exponentially, which can lead to an explosion.

# Difference in reaction heat of plasma and classic polymerization

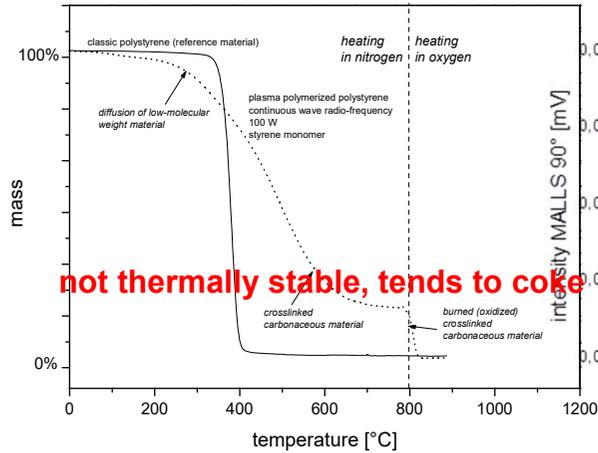
Energy per molecule needed for polymerization (calorimetric data)



# Evidence for the irregular structure of plasma polymers from a chemical point of view

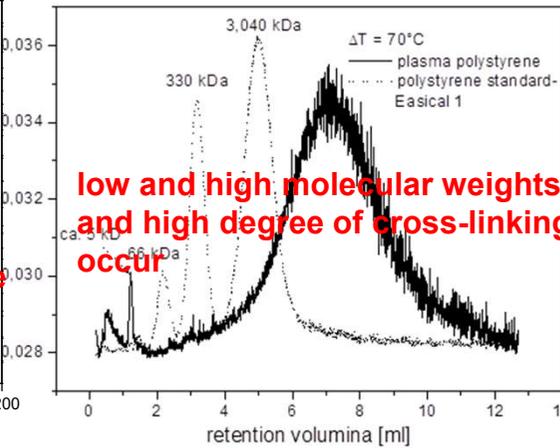
Plasma polymers have irregular structure and composition, therefore inferior mechanical and chemical properties

**Thermogravimetric analysis**



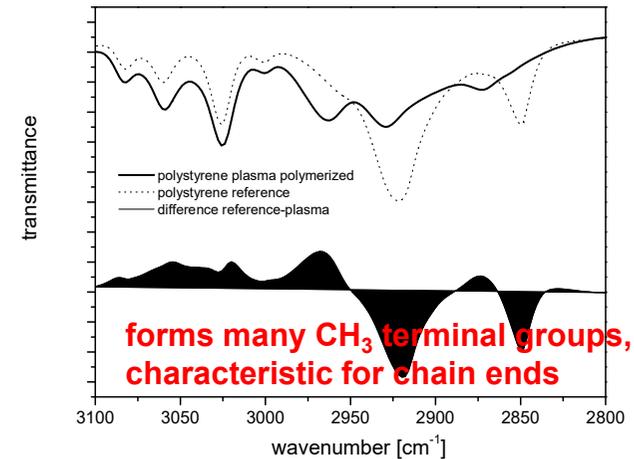
not thermally stable, tends to coke

**Thermal Field Flow Fractionation**



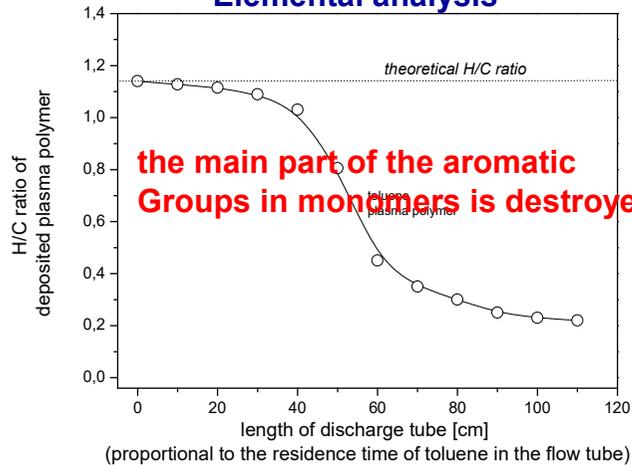
low and high molecular weights and high degree of cross-linking occur

**FTIR-ATR**



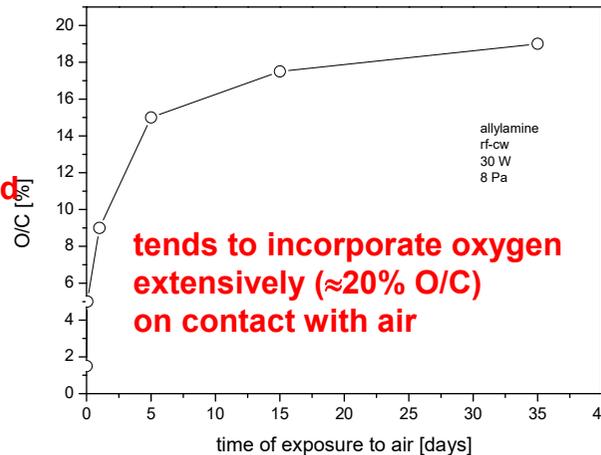
forms many CH<sub>3</sub> terminal groups, characteristic for chain ends

**Elemental analysis**



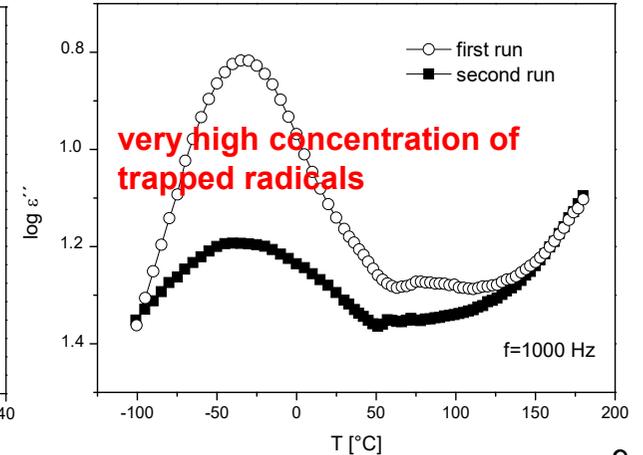
the main part of the aromatic Groups in monomers is destroyed

**Post-plasma oxygen incorporation measured by XPS**



tends to incorporate oxygen extensively ( $\approx 20\%$  O/C) on contact with air

**Dielectric Relaxation Spectroscopy**



very high concentration of trapped radicals

# What conclusions can be drawn from the comparison of the properties of plasma polymers and classical polymers?

More drawbacks than advantages

**Disadvantages** → bad chemical and mechanical characteristics dominate

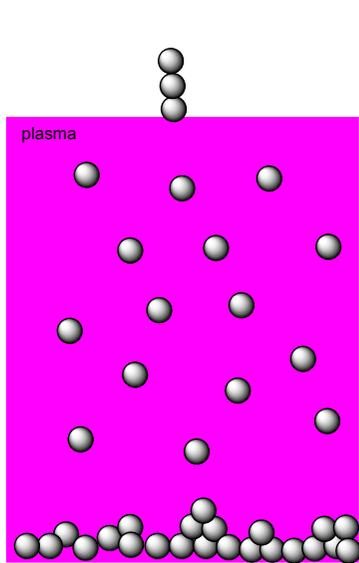
- ionization, dissociation, **fragmentation** of monomers/precursors dominates
- **random recombination** of atoms, radicals and fragments of the monomer molecule
- **hydrogen release** from monomers/polymers increases the electron temperature and intensifies the aggressiveness of the plasma
- **crosslinking** and polymer **decomposition** of deposited plasma polymer layers is additionally enhanced by irradiation with vacuum-ultra-violet from plasma
- radicals react by recombination and **radicals remain trapped** in the layer
- post-plasma radical-radical recombination (crosslinking) and **peroxidation** of trapped radicals by oxygen from air (auto-oxidation)
- long-term **ageing** of plasma polymers by peroxidation, oxidation of double bonds, radical-radical recombination
- **chain-growth polymerization in low-pressure discharges is not possible** because of low monomer density in vacuum or in air for prompt propagation of chain growth
- ethylene plasma polymers do **not have even the shortest regular sequence** of  $-\text{[CH}_2\text{-CH}_2\text{]}_2-$ , as evidenced by the absence of a rocking band at  $\rho\text{CH}_2 \approx 725 \text{ cm}^{-1}$  in the IR spectrum

**Advantages** → only monosort functionalized plasma polymers are of interest

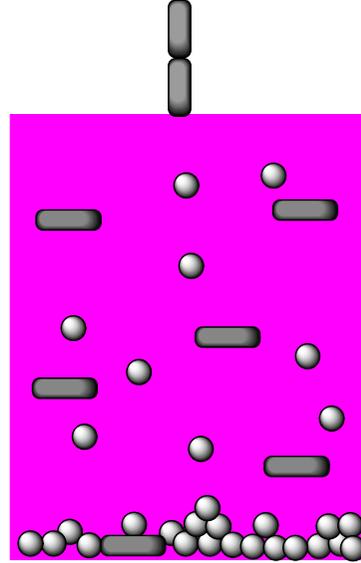
- **40-80% of the functional and reactive groups survive** the plasma polymerization process so that they can mediate adhesion or serve as an anchor point for the covalent grafting of functional molecules
- radical sites, post-plasma introduced O containing polar groups and **defects improve adhesion**

# New approaches to avoid the synthesis of irregularly structured polymer resins in plasma by introducing polymers instead of monomers into the plasma with its results

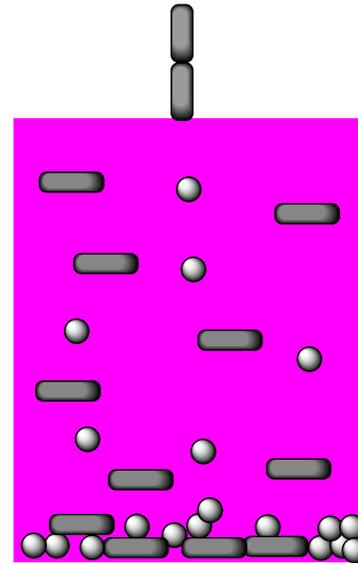
monomer/precursor vapor



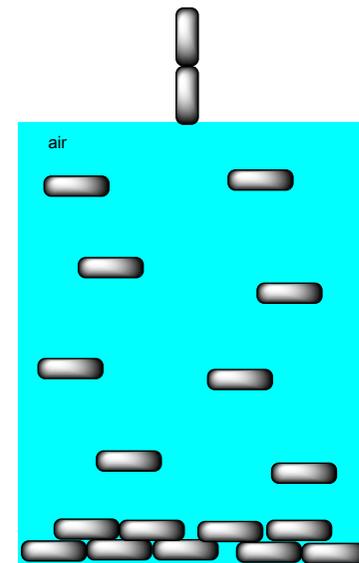
polymer solution



polymer solution



polymer solution



irregular structure



regular structure

Plasmapolymerization (dielectric barrier discharge or low-pressure glow discharge)

Polymer deposition via plasma (dielectric barrier discharge-DBD)

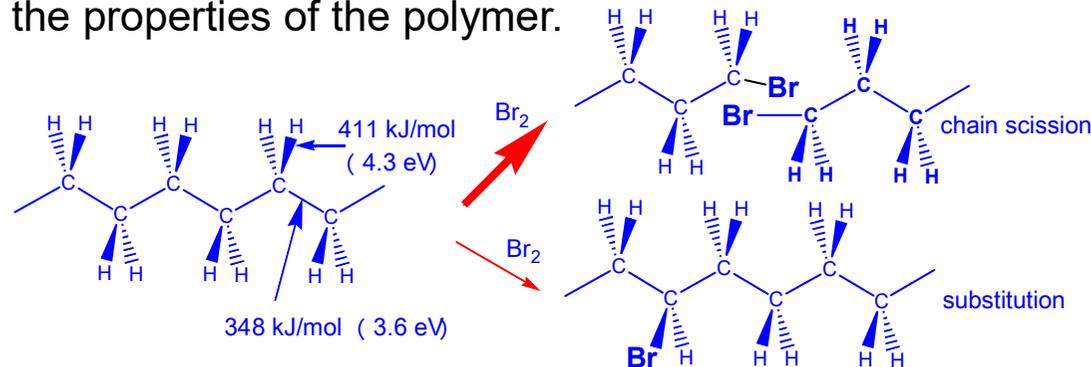
Deposition of nonpolar polymers via Atmospheric-Pressure Chemical Ionization (APCI)

Deposition of polar ionic polymers via ElectroSpray Ionization (ESI) **plasmaless**

# Following problems arise when classic high polymers are transferred to plasma

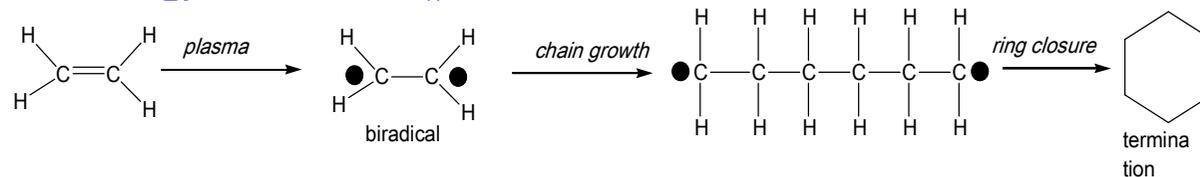
**First physical problem:** **Too high electron energy** and too high continuous energy supply

**First chemical problem:** The **C-C bonds in polymers are weaker than the C-H bonds, which leads to preferred scission of the polymer chain** on exposure to the plasma. Chain scission is associated with a decrease in molecular weight, which in turn means a dramatic deterioration in the properties of the polymer.



- C-C chains are (theoretically) more likely to be scissioned (fragmented) than C-H bonds
- polymer chains are primarily scissioned
- polymer degradation must occur
- networks must be formed
- radicals are formed → post-plasma oxidation
- selectivity is very low because of small differences in binding energies

**Second problem:**



**Third problem:** Polymers **cannot be evaporated** otherwise pyrolysis (chain scission) occurs.

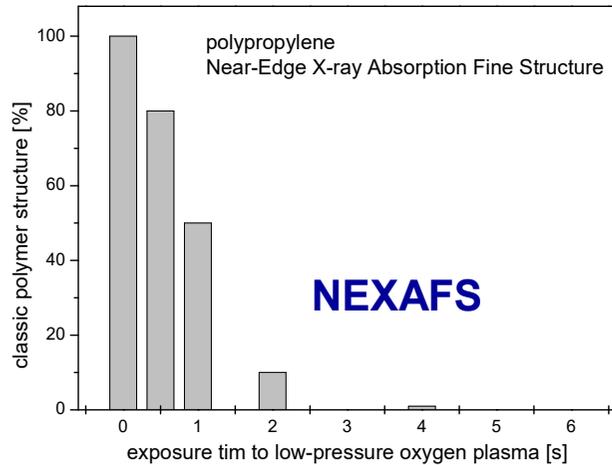
**Fourth problem:** Soluble polymers can be sprayed and transferred to air undecomposed

**Fifth problem:** Plasma **vacuum UV radiation generates cross-linking** in deposited polymer

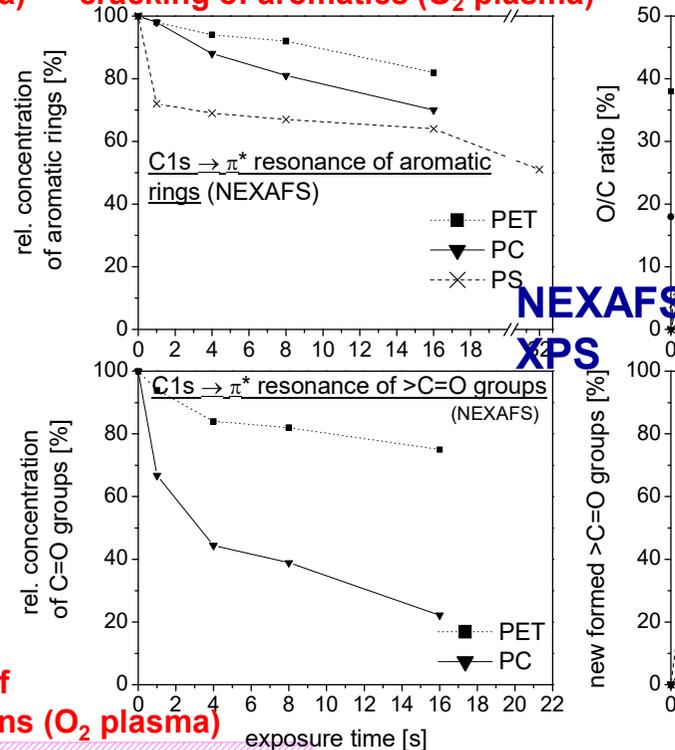
**Sixth problem:** Chain scission and H-abstraction generate **C-radicals** that can later react with atmospheric oxygen (auto-oxidation)

# Do the classical polymers retain at least part of their regular structure after they have been passed the continuous-wave plasma? Only partially or not at all?

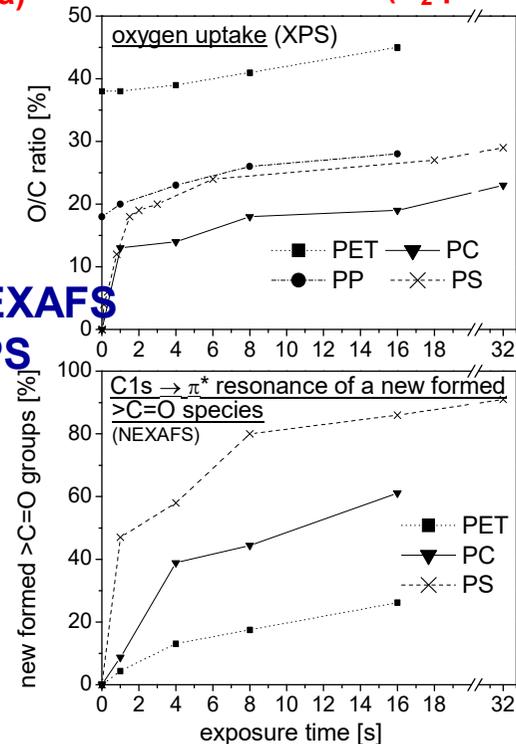
crystalline structure goes down (O<sub>2</sub> plasma)



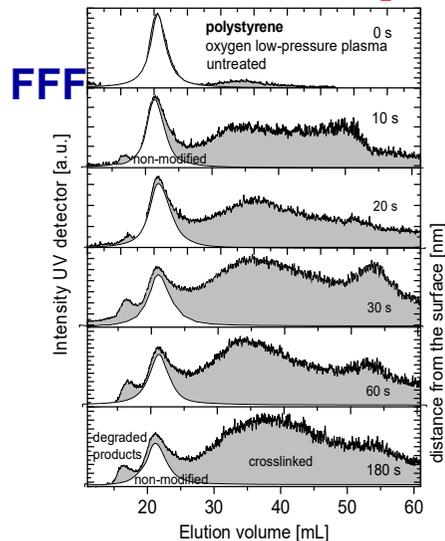
cracking of aromatics (O<sub>2</sub> plasma)



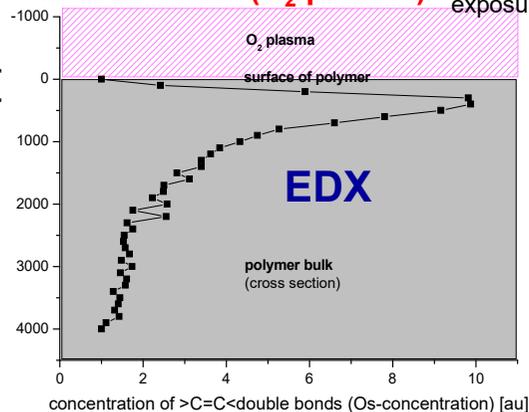
oxidation increases (O<sub>2</sub> plasma)



rapid crosslinking (O<sub>2</sub> plasma)

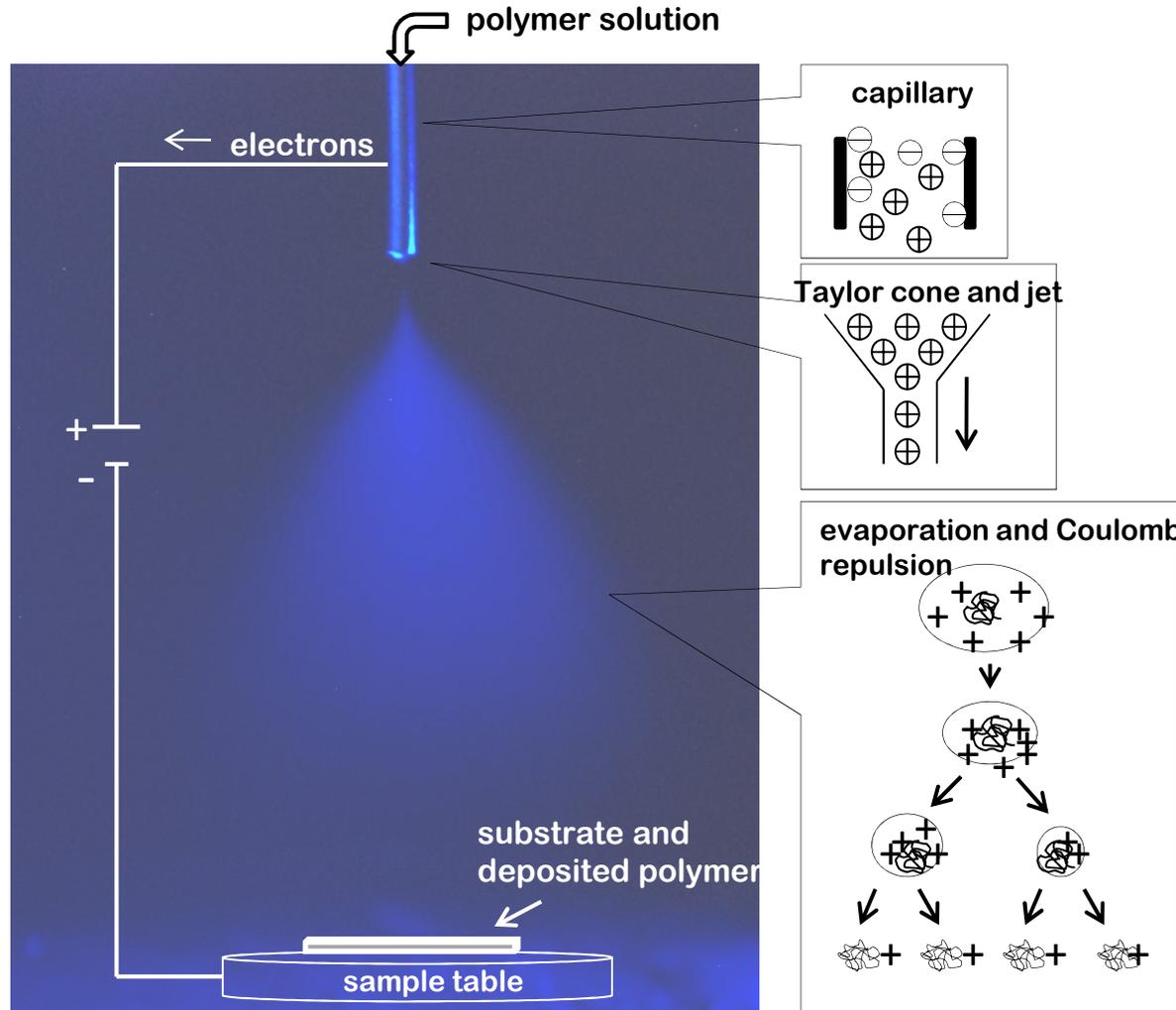


formation of unsaturations (O<sub>2</sub> plasma)



Therefore, the chance of forming regularly structured plasma polymers by introducing classic high polymers instead of monomers into the plasma and partial preservation of **regularly structured sequences is low**. In addition to the plasma particle bombardment, the extensive and high-energy **plasma vacuum UV radiation** is primarily responsible for the destruction of any original regular structure.

# Deposition of a monomolecular layer of single macromolecules by electrospray ionization (ESI) in atmosphere



## Mechanism

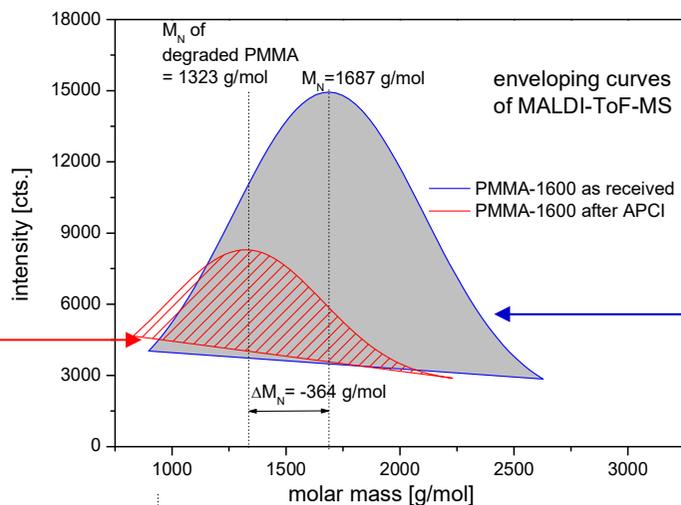
- The droplets of a polymer spray formed by a capillary are positively charged
- The droplets repel from another because of equal (positive) charge
- The droplets lose solvent on their way to the counter electrode
- Therefore, the diameter of droplets shrinks
- Then, equal charges come together
- The result is that Coulomb explosions lead to fission of droplets
- Smaller droplets are formed
- In a cascade of such fissions separation of single macromolecular ions is possible
- These single charged polymer ions are discharged at counter electrode and are deposited as mono- (poly-) molecular layer

# Limited retention of regular polymer structure using PMMA and APCI

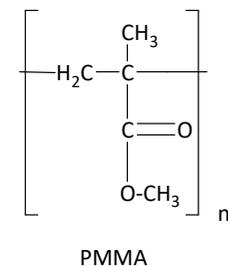
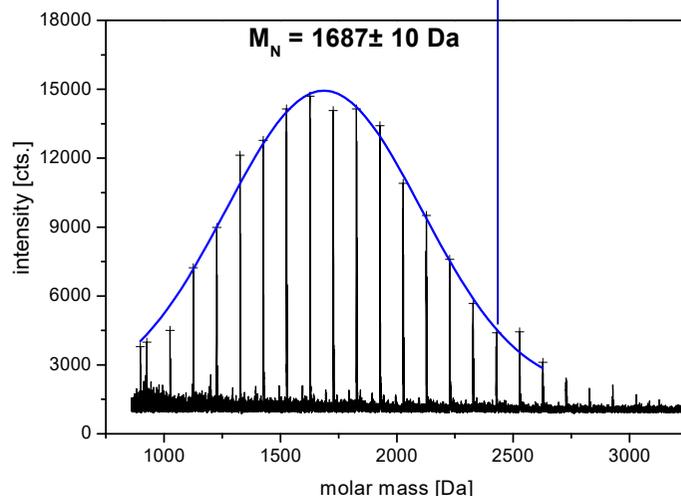
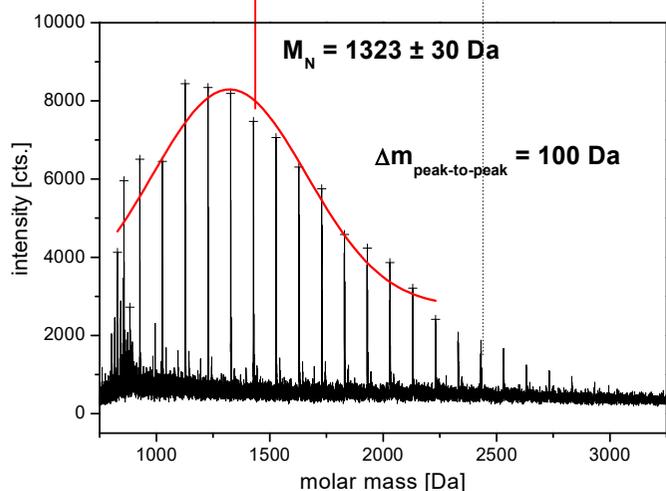
Some poly(methyl methacrylate) (PMMA) sequences remain intact during short-term treatment with **atmospheric pressure plasma chemical ionization (APCI)** in air



plasma glow at top of ESI capillary



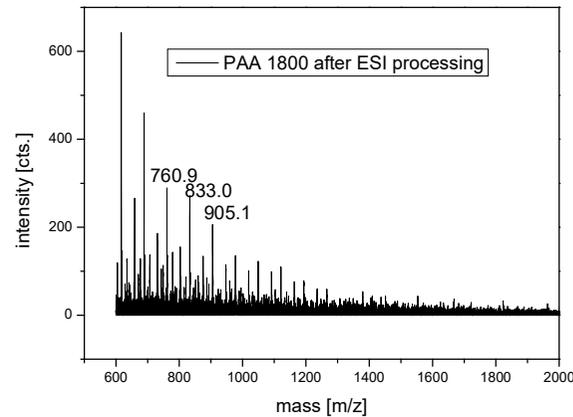
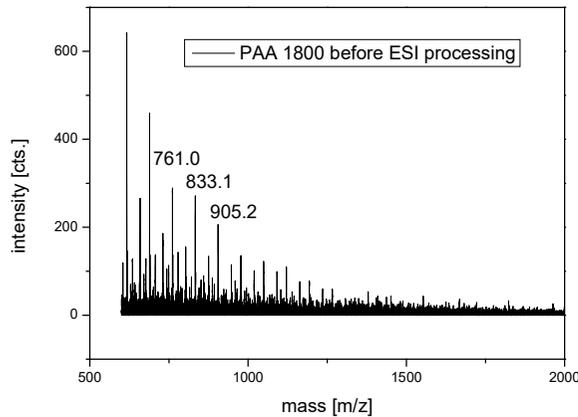
- APCI-deposition (= ESI + plasma) of PMMA with plasma-activation:**
1. Number-average of molecular weight decreases by 21%
  2. Intensity decreases by 50%



MALDI-ToF (Matrix-Assisted Laser Desorption Ionization - Time of Flight) mass spectra of PMMA before (right) and after (left) APCI deposition

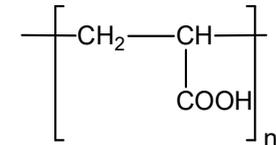
# Complete retention of the original structure of the poly(acrylic acid) (PAA) layer when using **plasmaless electro-spray ionisation (ESI)**

No changes in structure and composition are detected

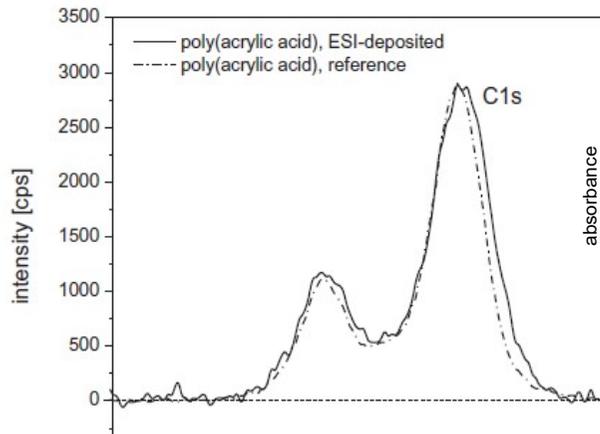


**MALDI** (Matrix-Assisted Laser Desorption Ionization) mass spectra of poly(acrylic acid = PAA) before and after ESI (Electro-Spray-Ionization) deposition **are identical**

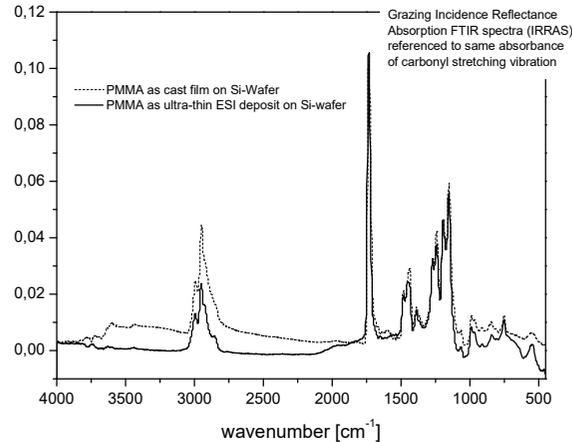
poly(acrylic acid)



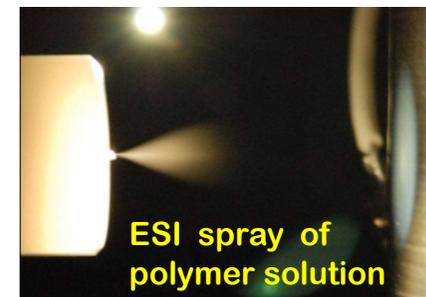
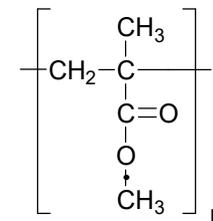
No differences in spectra of reference polymers and ESI-sprayed polymers



**XPS C1s peaks** of poly(acrylic acid) deposited as **identical** layers by casting and by ESI with thickness of <10 nm



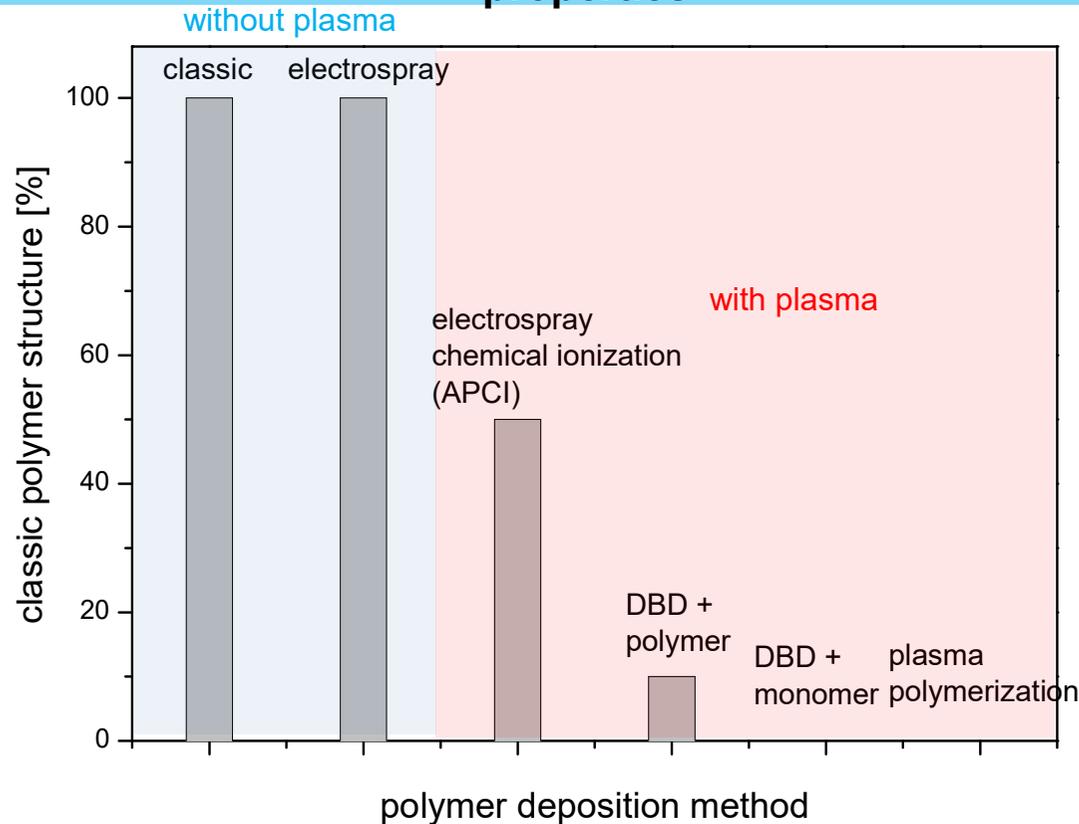
**IRRAS** (Infrared Reflection Absorption Spectroscopy) spectra of poly(methyl methacrylate = PMMA) before and after ESI (Electro-Spray-Ionization) deposition **are identical**



**ESI spray of polymer solution**

# How high is the proportion of remaining regular classical polymer structures after plasma exposure?

The classic polymer structure is largely destroyed, resulting in significantly deteriorated properties



J. B. Fenn  
1917-2010  
Nobel price 2002  
ESI

1. **Plasma polymerization**, starting with classic monomers, **does not generate any regular structure**
2. Starting with **high polymers** instead of monomers it is evident that any plasma exposure rapidly **destroys nearly all regular polymer sequences and structures**
3. **Conclusion:** Polymer layers with a **classic chemical structure and correspondingly high-quality physical and chemical properties** can only be achieved **without plasma**

# What conclusions can be drawn from the comparison of the properties of plasma polymers and classical polymers?

## To mechanism - disadvantages

1. Any impact of a plasma on polymers **destroys** their structure and composition (“atomic bomb”)
2. Plasma chemical reactions of **organic monomers** and polymers are **non-selective** and lead to **many different products** within the polyrecombination during layer deposition
3. Degradation reactions, but also cross-linking of polymers, lead disproportionately to serious **loss of properties**, i.e. every polymer layer that has seen plasma is inferior in its properties
4. The **C-C bonds** in polymers are somewhat easier to cleave than the **C-H** bonds. This leads to chain degradation when exposed to plasma and thus to serious losses in mechanical strength
5. The fragments and radicals generated by the plasma cannot be completely saturated during layer deposition, radicals are trapped, retain their reactivity over long periods of time and react with atmospheric oxygen to form all conceivable O-functional groups as part of so-called **auto-oxidation**, therefore, plasma polymers **are not stable**

## Layer formation - open questions that spontaneously come to mind

6. Interactions between plasma-activated surface and plasma polymer and their radicals **have not been investigated** but may be **beneficial** for higher adhesion
7. Are monomolecular plasma polymer coatings (approx. 1 nm) free of pin holes?

## Attempts to introduce chemically regular and selective processes

8. Pulsed and pressure-pulsed plasma were hardly successful
9. The **bromination** was selective, oxygen incorporation was prevented, but degradation at surface

## Successful attempts to obtain a regular polymer structure

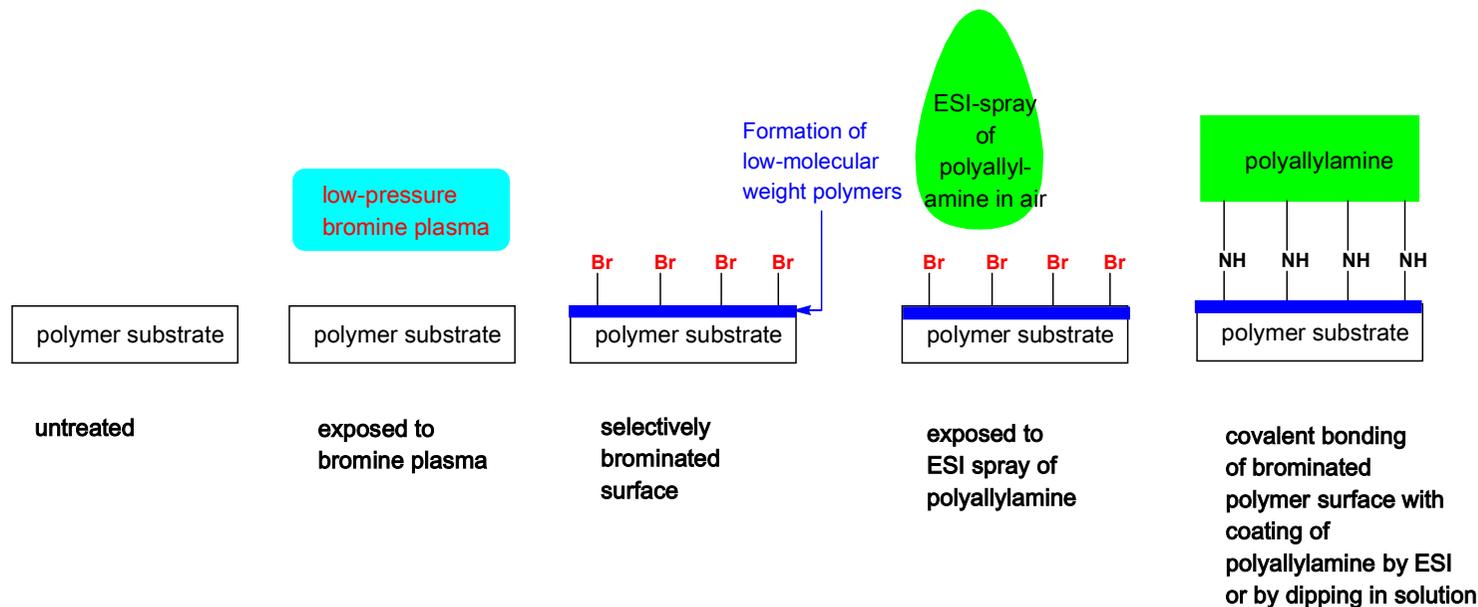
10. **Electrospray-ionization (ESI)** deposition of ultra-thin regularly structured polymer layers have **regular structure and composition**

# Why can a plasma still be useful in the deposition of well-adhering ultra-thin polymer layers with a regular structure?

The plasma can break every chemical bond

**Conclusions** for a sensible use of plasma, also taking into account the plasma-induced post-tidal structural changes of polymers shown by an example:

**Plasma bromination** of polymer substrates and **electrospray ionization coating with reactive classical polymers** as a useful application of a plasma in the deposition of **covalently adhering thin polymer layers on polymer substrates**



## Advantages

- Plasma bromination is almost 100% selective
- *Monomolecular layers of the polymer can be deposited using the ESI process*
- Very strong covalent bonds are formed at high density:  $\blacksquare\text{-Br} + \text{H}_2\text{N-}\sim\rightarrow\blacksquare\text{-NH-}\sim + \text{HBr}$
- This post-plasma chemical reaction takes place spontaneously and requires no additional energy
- Coating can be carried out in air

## Disadvantages

- Plasma bromination leads to degradation on the polymer surface
- A weak boundary layer is formed, not resistant in solvents
- Bromination is carried out in a low-pressure plasma (vacuum process)