Supramolecular Polymerization


E.W. Meijer

- 1982: PhD from University of Groningen (Prof. Wynberg)
- 1982-1989: Research scientist with Philips Research
- 1989-1992: Research scientist with DSM Research
- Since 1992: Professor in organic chemistry at Eindhoven University of Technology and Head of the Laboratory of Macromolecular and Organic Chemistry

- Recipient of many awards, particularly the ACS Award in Polymer Chemistry in 2006 and the prestigious SPINOZA-Award of the Dutch Science Foundation NOW in 2001
- Member of many editorial advisory boards, including Chemical Communications and Angewandte Chemie
- Two companies started from his research activities (SyMO-Chem in 2000 and SupraPolix in 2003)
Research Interests

- Self-assembled π-conjugated systems
- Supramolecular polymers and helical architectures
Polymers – Brief Definition History

- **1833**: Berzelius defined the word **Polymer** to recognize the fact that two compounds may have the same composition but different molecular weights.

- **1920**: Staudinger propose that polymeric substances are long chains of short repeating units linked by covalent bonds.

- **1931**: Carothers classified macromolecules by types of compounds that are capable of polymerizing and by the types of polymerization.
**Polymers – Brief Definition History**

**POLYMERIZATION**

WALLACE E. CAROTHERS

Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

Received March 21, 1931

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**Classification still used today**

**Importance of supramolecular interactions within polymer science**

**Are macromolecules required to obtain polymer materials?**
Supramolecular Polymers

“Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions, resulting in polymeric properties in dilute and concentrated solution as well as in the bulk. The directionality and strength of the supramolecular bonding are important features of systems that can be regarded as polymers and that behave according to well-established theories of polymer physics” in Chem. Rev. 2001, 101, 4071.

Figure 1. Schematic representation of a covalent polymer (a); and a supramolecular polymer (b).
Supramolecular Polymers

- 3 possible classifications:
  - Physical nature of the noncovalent force that lies at the origin of the reversible interaction (hydrogen bonds, π-π interactions, hydrophobic interactions, metal-ligand bindings)
  - Type of monomer(s) used (single monomer with either self-complementary or complementary end-group interactions or two different bifunctional monomers containing only one type of interaction)
  - Evolution of the Gibbs free energy of the polymer as a function of conversion, so-called thermodynamical classification
# Supramolecular Polymers

<table>
<thead>
<tr>
<th>« Conventional » Polymerisation</th>
<th>Supramolecular Polymerisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Kinetic control because of the potential barrier of the back reaction</td>
<td>• Thermodynamic control</td>
</tr>
<tr>
<td>• No dilution effect on the molecular weight or on the conversion</td>
<td>• Extent of reaction directly coupled to thermodynamic forces such as $[C]$, $T$ and $P$</td>
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The diagrams illustrate different types of polymerisation:

- **a)** Isodesmic polymerisation
- **b)** Ring-Chain polymerisation
- **c)** Cooperative polymerisation
Supramolecular Polymers

ISODESMIC SUPRAMOLECULAR POLYMERIZATION
Definitions

*Isos:* equal  *desmos:* bond

(a) isodesmic supramolecular polymerization of a rigid discotic molecule into a linear supramolecular polymer;

(b) isodesmic supramolecular polymerization of a bifunctional monomer in which the two binding groups are connected via a flexible spacer.

\[
\begin{align*}
M_i + M_j & \overset{K}{\rightleftharpoons} M_{i+j} & [M_i] = K_i [M_j]^i \\
M_{i+j} + M_j & \overset{K}{\rightleftharpoons} M_{i+2j} & [M_i] = K_i^2 [M_j]^2 \\
\vdots & & \\
M_{i+\ell} + M_j & \overset{K}{\rightleftharpoons} M_{i+\ell+j} & [M_i] = K_i^{\ell} [K_j]^{\ell} & i = 1, 2, \ldots, \infty
\end{align*}
\]
Examples (1)


- Substitutions at the bay position lead to decrease in K
- $K(31) < 3$ orders of magnitude $K(27)$
- Isodesmic model fits with UV changes observed for 27 and 31
- When substituents at bay positions, only dimerization occurs (32-35)
- 36: Dimer at high T and P-type polymer at lower T

Examples (2)

1990: Introduction of the concept of (main-chain) supramolecular polymer by Lehn

Systems studied by variable $^1$H NMR and TEM $=>$ fits with theoretical model on isodesmic polymerization

Isodesmic Supramolecular Polymerization

Examples (3)

Viscous in CHCl₃ at 40 nM

Chain Stopper

DPₙ = 700 at 40 nM

Isodesmic Supramolecular Polymerization

Examples (4)

Inclusion complexes


- Encapsulation of ditopic molecules (solvent, \(p\)-difluorobenzene)
- \(K(51)\) determined by FRET studies
  => useful technique for \(K\) calculation at low concentration
- Polymeric assemblies preserved with sulfonyl urea and heterodimer

\[
\begin{align*}
51 & : R_1 = R_2 = C_3H_7, & R_3 = R_4 = C_6H_{14}p-CH_3, & X = p-C_6H_4 \\
52 & : R_1 = R_2 = C_{10}H_{21}, & R_3 = R_4 = C_6H_{14}p-CH_3, & X = p-C_6H_4 \\
53 & : R_1 = R_2 = C_3H_7, & R_3 = R_4 = C_6H_{14}p-C_6H_{15}, & X = p-C_6H_4 \\
54 & : R_1 = R_3 = C_{10}H_{21}, & R_3 = R_4 = SO_2C_6H_{14}p-CH_3, & X = (CH_2)_{16} \\
55 & : R_1 = R_3 = C_3H_7, & R_3 = C_6H_{14}p-C_6H_{15}, & X = p-C_6H_4 \\
& & R_4 = SO_2C_6H_{14}p-CH_3
\end{align*}
\]

Coulombic interactions

Schmuck, C. *Tetrahedron* 2001, 57, 3063

Metal-ligand interactions


\[
\begin{align*}
\text{Coordination Polymers in DMSO}
\end{align*}
\]
Conclusions

- No need to adopt a high-energy conformation to allow for incorporation into the supramolecular polymer – the orientation of all the bonds in the molecule is independent of its position in the supramolecular polymer.

- Prerequisite for the isodesmic polymerization: No influence of the binding of one end group to another on the reactivity of the other end group connected to the same spacer.
Supramolecular Polymers

RING-CHAIN SUPRAMOLECULAR POLYMERIZATION
Definitions

Reversible polymerization of a ditopic monomer in which each linear aggregate (including the monomer) in the assembly pathway is in equilibrium with its cyclic counterpart.

2 reversibly associating end groups connected via a flexible hydrocarbon tether

Concept of effective concentration
Because end group A cannot escape from the sphere of radius $l$, equal to the full length of the chain, end group B experiences an effective concentration of A. If this effective concentration is higher than the actual concentration of A end groups in solution, intramolecular association between A and B is favored.

Effective Molarity
Limit concentration of the monomer below which cyclisation is more favored than oligomerisation

$EM = \frac{K_{\text{intra}}}{K_{\text{inter}}}$
Examples (1)


Enthalpically driven supramolecular polymerisation

Entropically driven ring opening polymerisation

Examples (2)

1998: 1rst pseudo-rotaxane polymerisation reported by Stoddard et al.

Alternating arrangement of the two monomers
Critical concentration at 40nM (viscosity)

Influence of the linker size

Gibson, H.W.; Yamaguchi, N.; Jones, J.W.

Wang, F.; Han, C.; He, C.; Zhou, Q.; Zhang, J.; Wang, C.;

Ring-Chain Supramolecular Polymerization
Examples (3)

Selective formation of cyclic species using a coordinating solvent and low concentration

Only linear species

Preorganization due to the rigid linker


Ring-Chain Supramolecular Polymerization

Supramolecular Polymers

COOPERATIVE SUPRAMOLECULAR POLYMERIZATION
In contrast to isodesmic supramolecular polymerizations, cooperative supramolecular polymerizations are characterized by at least two different association constants ($K_n < K_e$) in the assembly pathway and by a critical concentration or temperature at which the supramolecular polymer starts growing.

**Differences with isodesmic polymerisation:**

- Time-dependant lag in the formation of the polymer
- Lag abolished by addition of preformed nucleus
- Critical C or T representing the monomer in equilibrium with the supramolecular polymer (when polymer starts growing)
Thermodynamic Aspects

Degree of cooperativity $\sigma = K_2/K$ (limitation: nucleus = dimer)

Below critical $C$, almost no polymeric species

At critical $C$, no increase in monomer concentration but increase in equilibrium concentration of supramolecular polymers

Growth chain occur above critical $C$, and high $M_W$ polymers obtained over small $C$ range

Bimodal mass distribution

Cooperative Supramolecular Polymerization
Molecular Origin of Cooperative Growth

- Electronic effects (short-range polarization and long-range electrostatic effects) mainly encountered in linear polymers that polymerize via H bonds

- Structural effects (helix formation and allosteric conformation changes)

- Hydrophobic effects (tendency for nonpolar solutes to aggregate in aqueous solution)
General Molecular Mechanisms

a) Single stranded helical supramolecular polymers

Generic allosteric model

\[ K_n \quad \leftrightarrow \quad K_L \]

\[ K_C \quad \leftrightarrow \quad K_H \]

\[ K_{LL} \quad K_{HH} \quad K_{HL} \quad K_{LH} \]

b) Multistranded helical or tubular structures. The red arrows indicate the secondary interactions responsible for the cooperative growth.

\[ K_n \quad \leftrightarrow \quad K_H \]

\[ K_C \quad \leftrightarrow \quad K_{HH} \]

\[ 1/K_C \quad K_{HH} \quad K_{LH} \quad K_{LH} \]

Cooperative Supramolecular Polymerization
Examples (1)

**Long rigid fibrilar structures**

![Chemical structures](attachment:image.png)

**Chain Stopper**

![Chemical structure](attachment:image.png)


**Origin of cooperativity:**

Polarization of the urea fonction after formation of dimers

Cooperative Supramolecular Polymerization
Cooperative Supramolecular Polymerization determined by T-dependant and solvent polarity dependent UV-vis spectroscopy
Addition of a chain stopper proves the reversibility of the polymerisation as shown by a decrease in viscosity
Nucleated polymerization mechanism proved when adding 130 to the achiral derivative
Examples (3)


One-handed quasi one-dimensional helical structures

![Chemical structure](image)

**High T**: Monomer and dimer (STM/NMR)

**Low T**: Polymer

Non sigmoidal transition

Introduction of helical twist leads to more favored polymerization

Cooperative Supramolecular Polymerization
Examples (4)

Ribbon-like Structures (π–π interactions and H bondings)


Non sigmoidal transition

Examples (5)


Different driving forces yield different arrangements in various solvents

Hydrophobic Effects

Cooperative Supramolecular Polymerization
Anti-Cooperative Polymerization

$K_n < K_e$

Anti-cooperative

Initial oligomerization energetically more favorable than subsequent elongation


Anti-Cooperative Supramolecular Polymerization
Anti-Cooperative Polymerization

$K_2 > K_e \text{ (NMR)}$

**Anti-cooperative**
Horne, W. S.; Stout, C. D.; Ghadiri, M. R.


**Cooperative**

Increase length when pH increase => Disrupt the balance between attractive and repulsive interactions

Dong, H.; Paramonov, S. E.; Aulisa, L.; Bakota, E. L.; Hartgerink, J. D.
FUNCTIONAL SUPRAMOLECULAR POLYMERS
Mechanical Properties

- With the proper choice of building blocks, properties similar to those of macromolecules can be obtained.

Self-Healing Properties

Electronic Properties

Amphiphilic Hexabenzocoronene Self-assembly in THF: nanotubes of 14nm wide

Resistance comparable to inorganic semiconductor nanotubes

Upon addition of a dense negatively charged hyaluronic acid (HA) solution onto a positively charged peptide amphiphile (PA) solution, the immediate formation of a solid membrane localized at the interface between the two liquids is observed. As the heavier hyaluronic acid sinks, the peptide amphiphile molecules engulf the negatively charged polymer, thereby creating a closed sac with the HA solution trapped inside the membrane.

CONCLUSIONS

• Three different mechanisms of formation of supramolecular polymers (isodesmic, ring-chain and cooperative)
• Supramolecular polymers possess many of the well-known properties of « traditional » macromolecules
• Dynamic nature allows adaptation of the supramolecular polymers to continuously changing surroundings
FUTURE CHALLENGES

- Control over monomer sequence and over the polydispersity of supramolecular polymers

- Achieve the level of sophistication of natural systems with artificial supramolecular polymers => development of supramolecular polymerizations operating under kinetic control (far from thermodynamic equilibrium)
Thanks for your attention

http://www.nicecarnaval.com/