

Rational design of organogelators and their use to create functional materials

U. Beginn, A. Koch, Y. Noppeney

ITMC / TexMC – Laboratory of Textile- and Macromolecular Chemistry

RWTH Aachen, Worringerweg 1, D-52056 Aachen, Germany

Phone: +49-241-80-28137, Fax: +49-241-80-22185, e-mail: uwe.beginn@texmc.rwth-aachen.de

‘Organogels’ are elastic- or viscoelastic materials consisting of organic solvents and low molecular weight organic ‘gelators’. The gelator forms three-dimensional networks of supramolecular structures confining the solvent. Very efficient gelation is found with gelator molecules that self-assemble to fibrous structures of large aspect ratios, e.g. rods or ribbons.^{1,2}

Though organogels are known since long³ new gelators are frequently not rationally designed, but obtained by chance. A simple rational concept to construct gel forming molecules is to prepare nearly flat, amphiphilic molecules consisting of small polar and bulky non polar parts.^{4,5} In a non polar environment the molecules will aggregate to minimise the contact between polar-, and non polar regions. According to this concept rod formation was found with tris(alkoxy)benzamides,⁴ N-sorbitoyl-3,4,5-tris(alkoxy)benzamides,⁵ and crown ether amphiphiles.⁶ The observed fibres were molecularly defined, and contained polar functional groups in their interior.

Bis[alkoxybenzoyl]semicarbazides (**1**, Scheme 1) are highly efficient organogelators that gel semi-polar, and non-polar organic liquids. In hexane, toluene, styrene, and 1,3,5-tri(isopropyl)benzene (TPB) the critical gelation concentration was below 0.7 wt% ($R = C_8H_{17}$). Gels arising from 3C-BS-8 ($X=1,4$ -phenylene, $R_1-R_3=C_8H_{17}$) and TPB exhibit shear thickening effects on exceeding concentrations of 0.2 wt% (see Figure 3) and cannot be molten below 220 °C.⁸

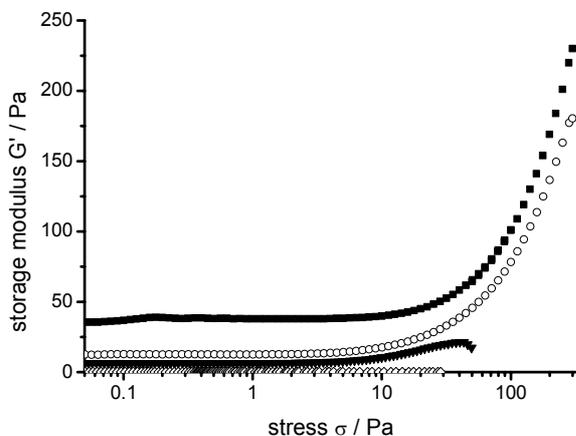


Figure 1: Storage modulus of gels from 3C-BS-8 in TPB (■: 0.75 wt%, ○: 0.5 wt%, ▼: 0.25 wt%, ◇: 0.12 wt%) (Bob-Couette, $\sigma = 0.1$ Pa, $\omega = 1$ rad/s, $T = 25$ °C)

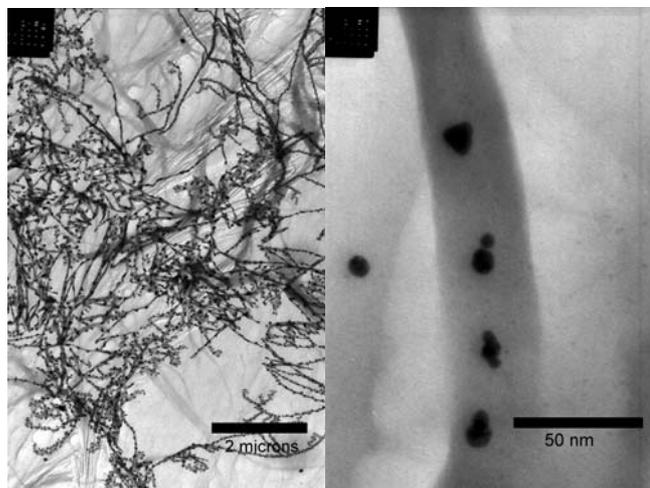
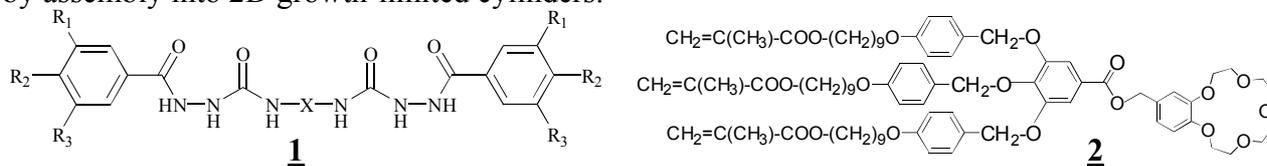


Figure 2: Gold nanoparticles mineralised in an organogel of 3CBS-8 (5 wt%) in toluene (left: overview, right: detail)

The high stability of semicarbazide gels make them valuable templates e.g. to generate “metallized organogels”. Such metallized organogels are precursors for the preparation of mesoporous metal networks, useful in electrochemistry, catalysis or electric shielding applications. Figure 2 depicts the morphology of a gel from 3BSC-8 in toluene where gold nanoparticles have been mineralised *in-situ*. The gelator formed fibres of 30 - 100 nm diameters that are covered with 10 – 20 nm gold nanoparticles.

The general persistence of the gelation abilities of the wedge shaped gelators against chemical modifications allows for the deliberate construction of gel-forming molecules to create functional materials. In particular the gelation of liquid monomers by polymerisable gelators, and subsequent

polymerisation of the gels offers a simple route towards macromolecular / supramolecular hybrid materials. One application of the hybrids is the construction of functional membranes: The macroscopic length the individual cylindrical ‘supramers’, consisting of preorganised monomer units, enables the generation of fibres exhibiting transport properties.⁶ Low molar mass type amphiphiles containing polymerizable units, e.g. **2** (Scheme 1) were developed to gel monomers by assembly into 2D growth-limited cylinders.^{6,7}



Scheme 1: Structure formula and the bis(semicarbazides) **1** ($R_i = H-, C_nH_{2n+1}O-$, $n = 8, 10, 12, 16$, $X = 1,4\text{-phenyl-}, 2,4\text{-toluyl-}, 2,6\text{-toluyl-}, 1,8\text{-naphthyl-}, 1,6\text{-hexyl-}$) and a polymerisable ion-channel forming gelator (**2**).

Photo-curing of the gel results in a crosslinked polymer with an embedded cylinder-network, covalently fixed to the polymer matrix (‘Matrix Fixed Supramolecular Channels’, cf. Figure 1).

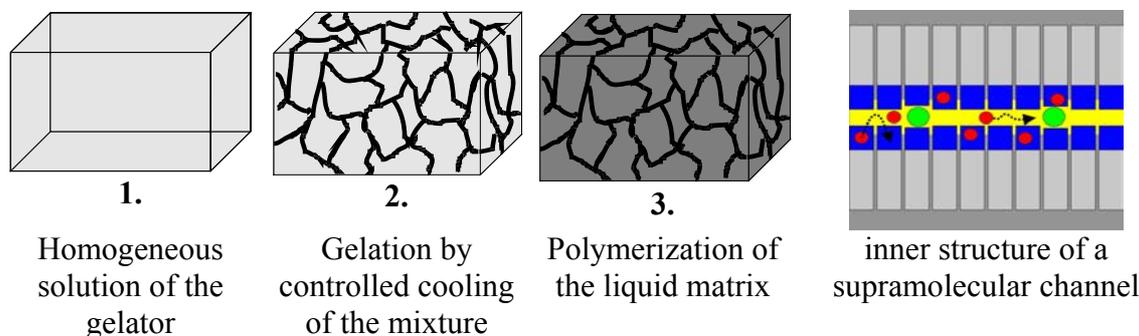


Figure 1: Schematically drawing of the ‘Matrix Fixed Supramolecular Channels’ process

In the centre of the cylinders the crown-ether moieties are stacked along the cylinder axis,⁶ forming a pathway for alkali metal ions. The supramolecular fibres of **1** were found to act as selective transport channels for alkali metal ions, transporting Li^+ -ions faster than Na^+ , and K^+ -ions. The observed ion selectivity is nearly independent of the ion concentration, and the transport properties react reversibly to temperature changes.⁷ The interactions between solid surfaces, and the lyotropic mesophase of **1** was used to orient the transport channels perpendicular to the plane of the membrane without the application of external electrical or magnetic fields. Due to the orientation the transport rates increased for one order of magnitude.⁷

Another application of semicarbazide gelators refers to the preparation of phase change materials to store latent heat, i.e. for thermal shielding of electronic devices.⁹

References:

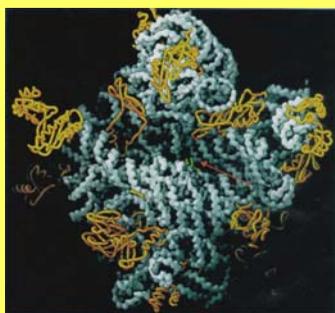
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- [2] P. Terech P., R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133.
- [3] A. Lipowitz, *Ann. Chem. Pharm.* **1841**, *38*, 348; M. O. Foster and T. Jackson, *Trans. Chem. Soc.*, **1907**, *91*, 1888.
- [4] U. Beginn, S. S. Sheiko, and M. Möller, *Macromol. Chem. Phys.*, **2000**, *201*, 1008.
- [5] U. Beginn, S. Keinath, and M. Möller, *Macromol. Chem. Phys.*, **1998**, *199*, 2379
- [6] U. Beginn, G. Zipp and M. Möller, *J. Polym. Sci. A: Polym. Chem.*, **2000**, *38*, 631; U. Beginn, G. Zipp and M. Möller, *Chem. Europ. J.*, **2000**, *6*, 2016.
- [7] U. Beginn, G. Zipp and M. Möller, *Adv. Materials*, 2000, **12**, 510-513; U. Beginn, G. Zipp, A. Mourran and M. Möller, *Adv. Materials* **2000**, *12*, 513-516.
- [8] U. Beginn, B. Tartsch, *Chem. Commun.* **2001**, 1924 – 1925.
- [9] U. Beginn, *Macromol. Mater. Eng.* **2003**, **288**, 245 – 251.

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U. Beginn, Y. Noppeney, B. Tartsch, L. Yan, X. Zhu



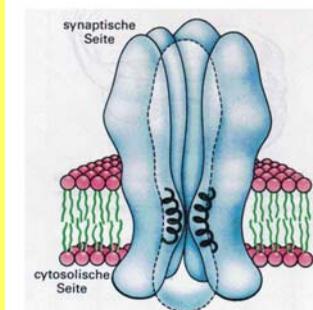
Biologic Growth-Limited Objects



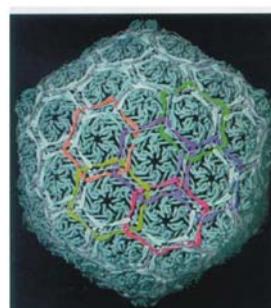
Ribosomes
Science **289**, 878 (2000)



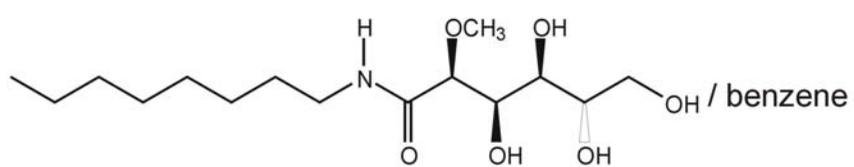
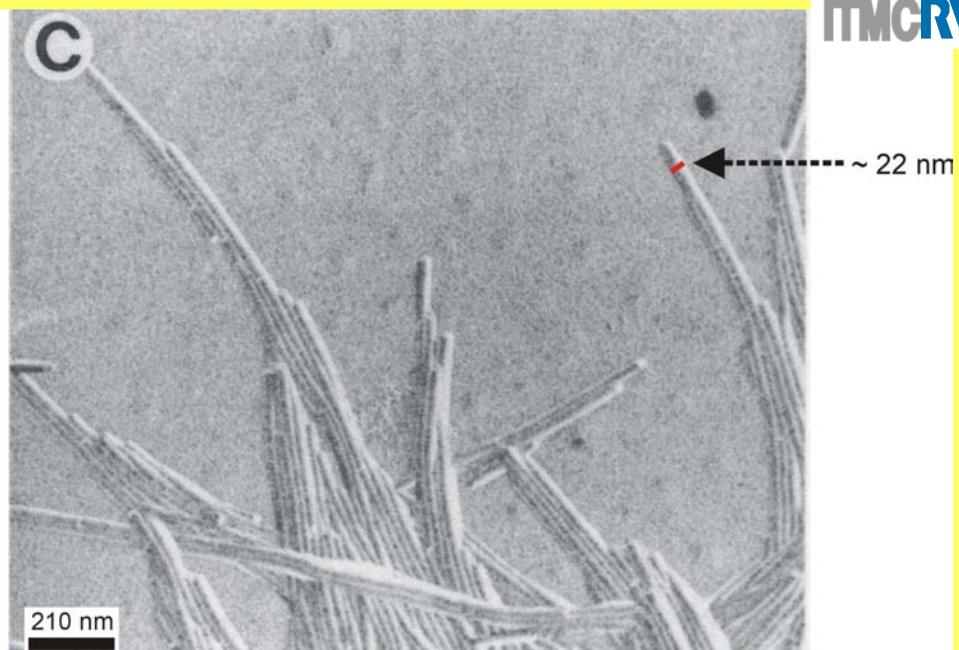
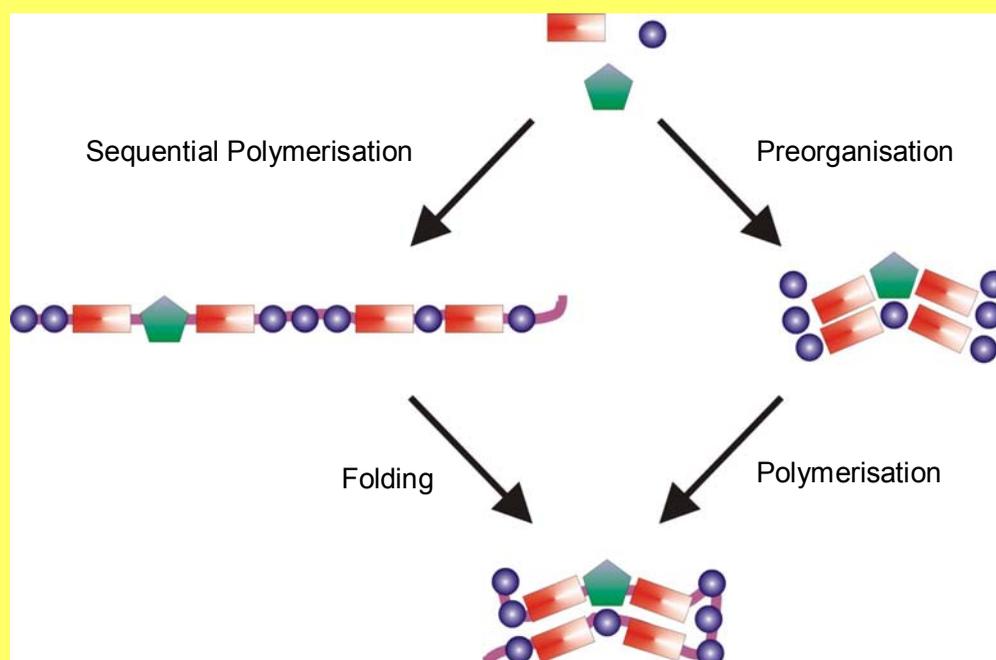
Chaperonines
Nature **402**, 693 (2000)



Membrane channels
Czihak, „Biologie“, 1981

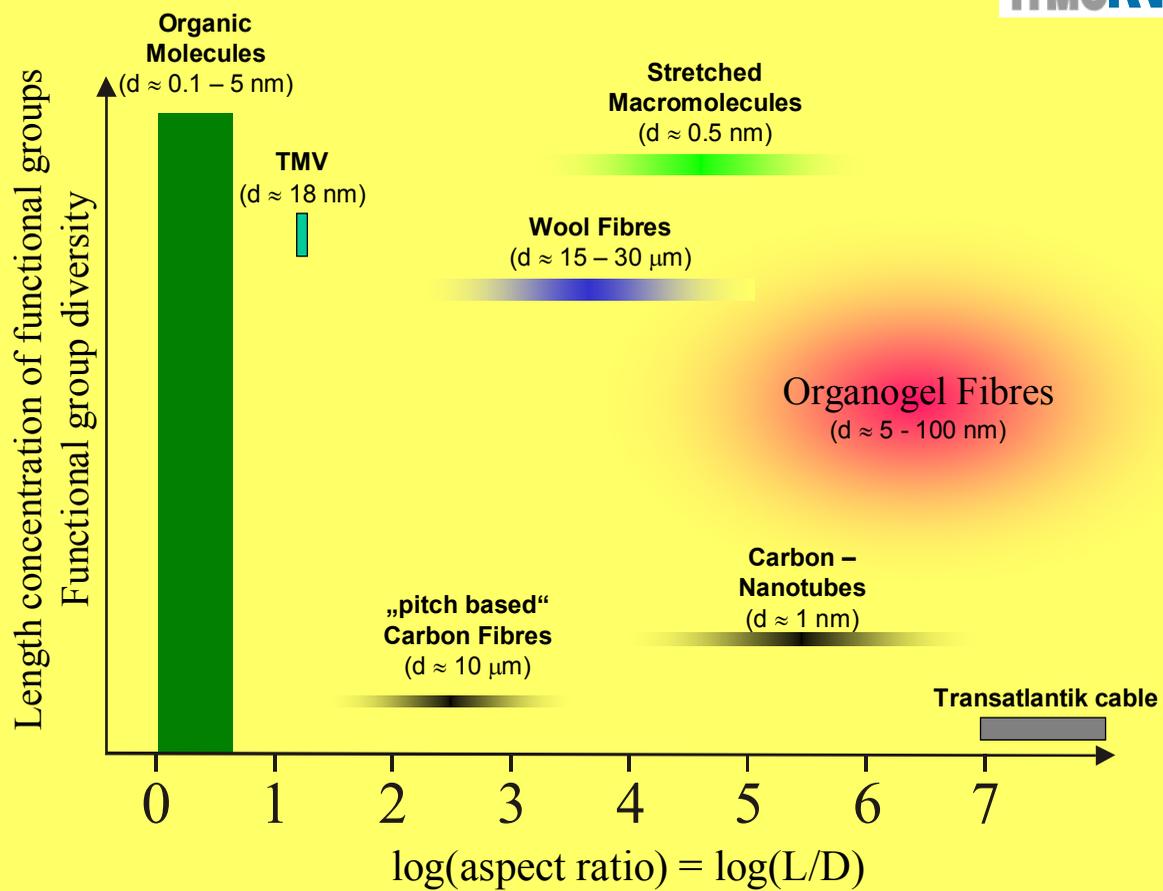


Virus shells
Science **289**, 2129 (2000)



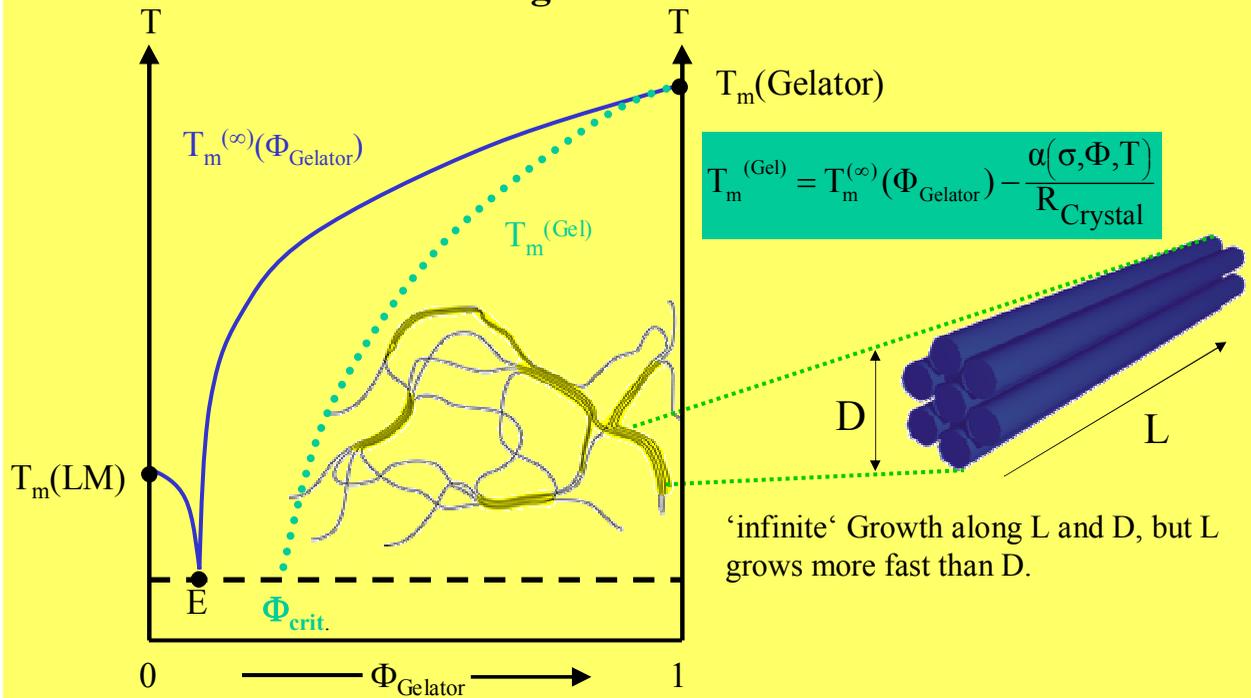
Organogels

Property	Application	Example	
		Industry	Academia
Thermoreversibility	„intelligent“ Thickeners	Lubricants, Inks, Ointments, Glues	Solid Electrolytes,
Thixotropy / Shear - thinning		Napalm, Paints	Solar Cells
Structural Definition	Supramolecular Chemistry	---	Templates, Tektones
Functionality	adaptive, switchable Materials	---	New Polymers, Functional Membranes



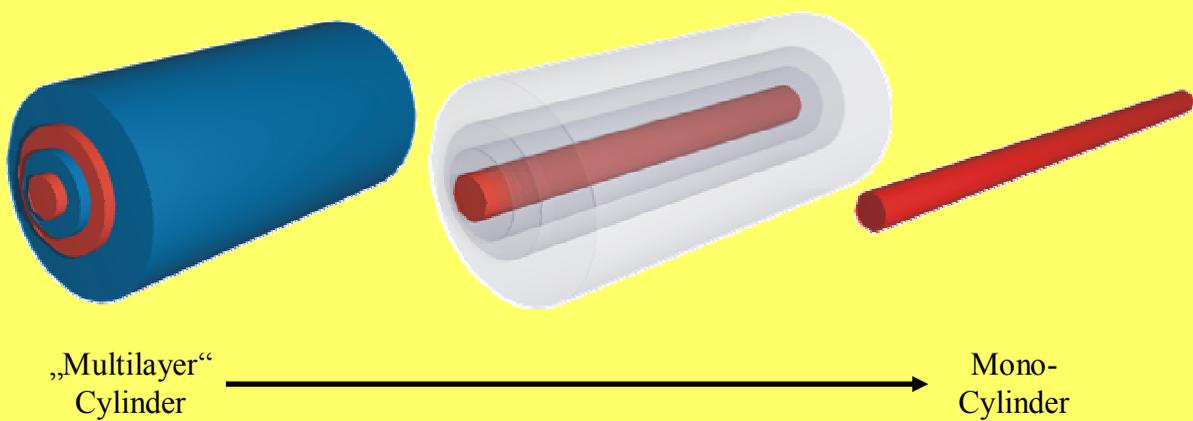
CRYSTALLIZATION

3D Ordering



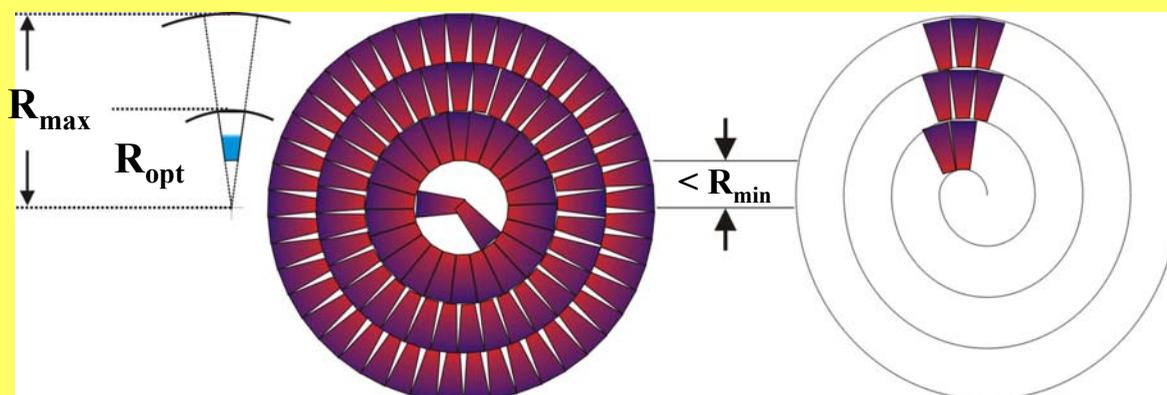
Kinetic Control of Crystallization Limits the Radial Growth and Yields Ultra-Fine Networks

Ultimative Structure Control



Monocyliner via Aggregation and total Inhibition of Radial Growth

Self - Limited Radial Growth



concentric Tubes

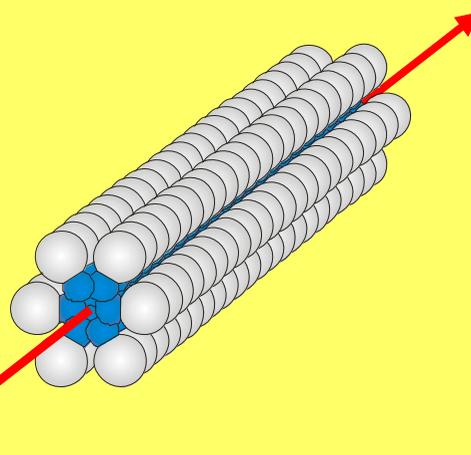
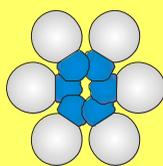
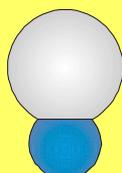
Rolled-up Layers

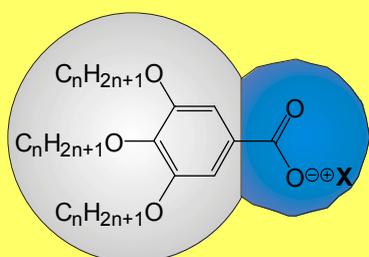
Cross-Section of Supramolecular Multilayer - Fibrils

Side view

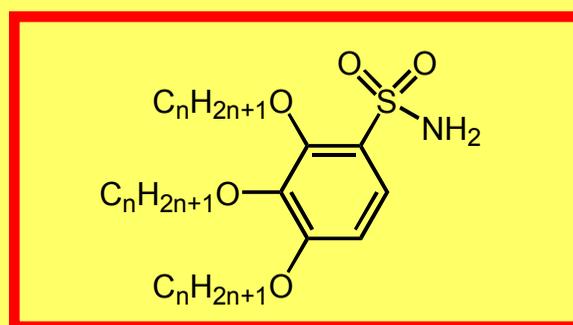
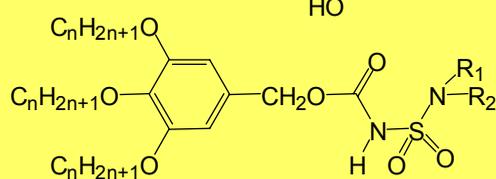
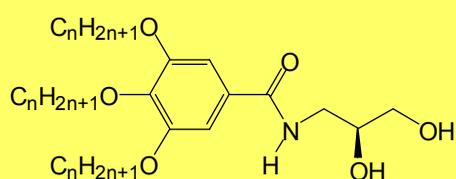
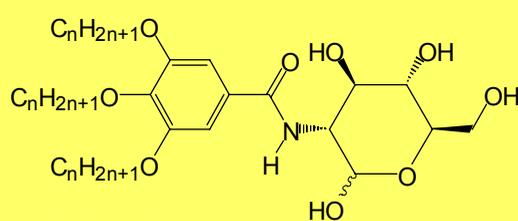
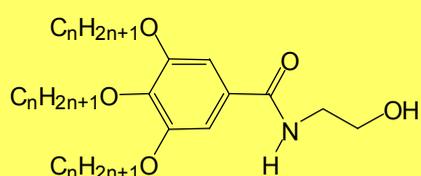
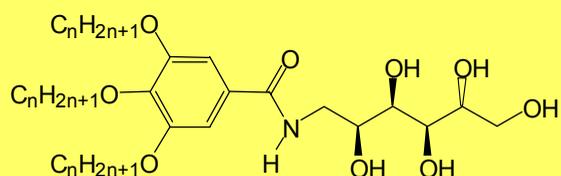
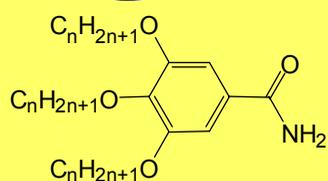


Top view

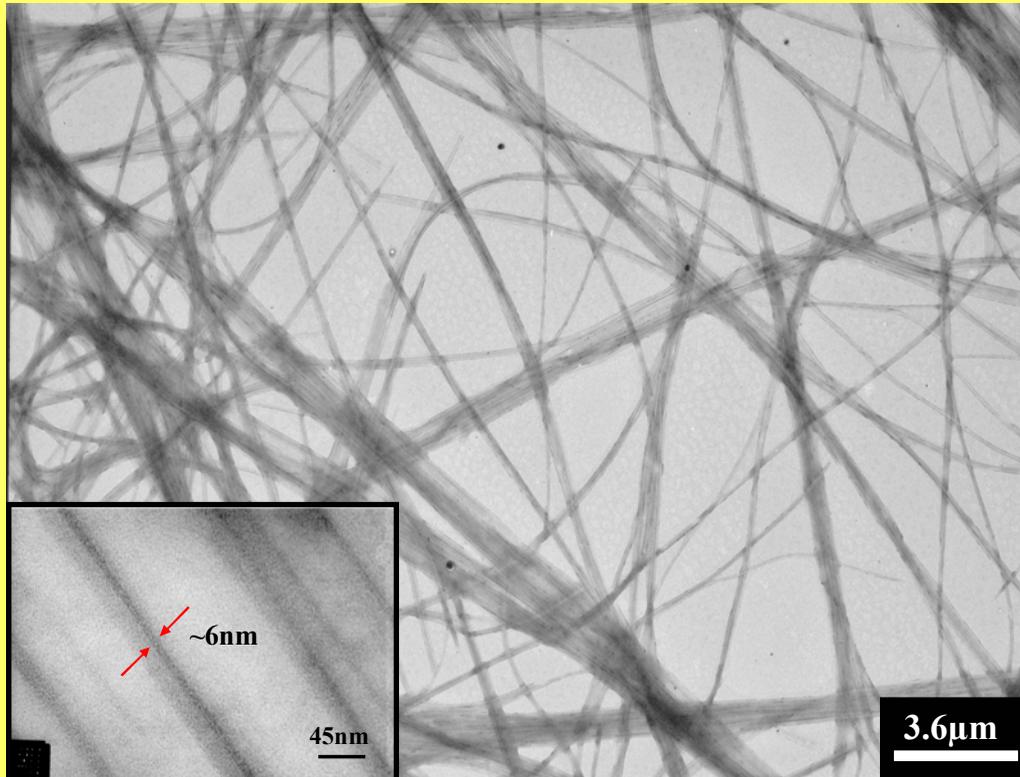




Wedge Shaped Amide – Gelators

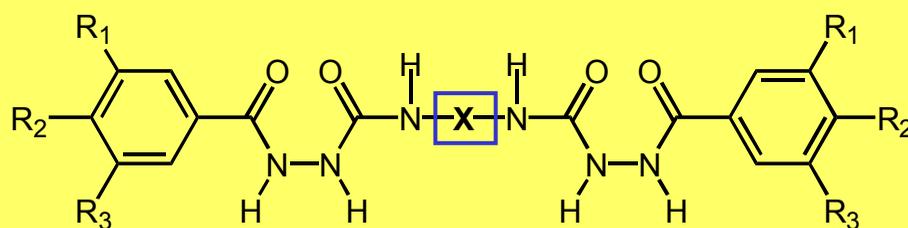
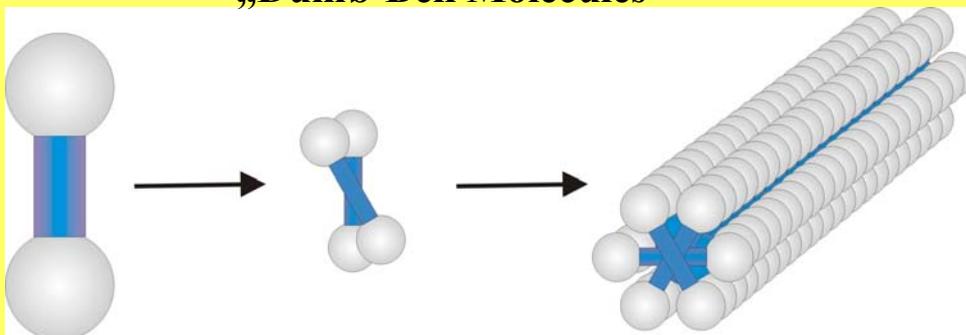


2,3,4-Tris(alkoxy)benzulfonamides

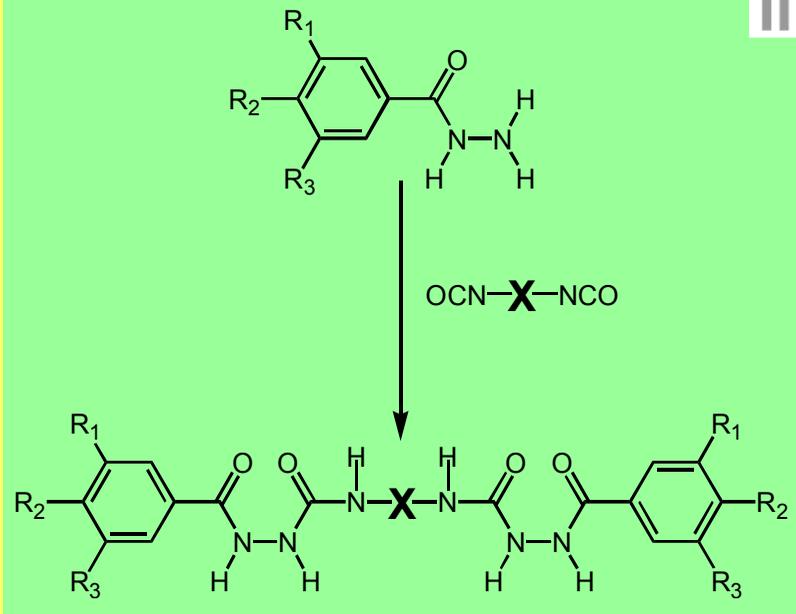


2 wt% 2,3,4-Tris(dodecyloxy)benzolsulfonamid in Styrene
(stained with RuO₄)

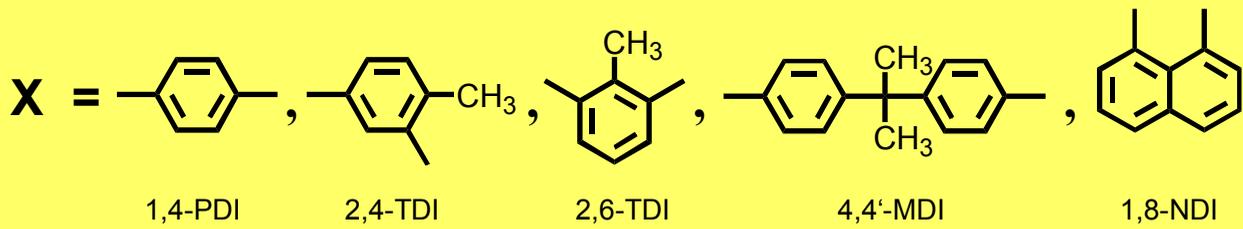
„Dumb-Bell Molecules“



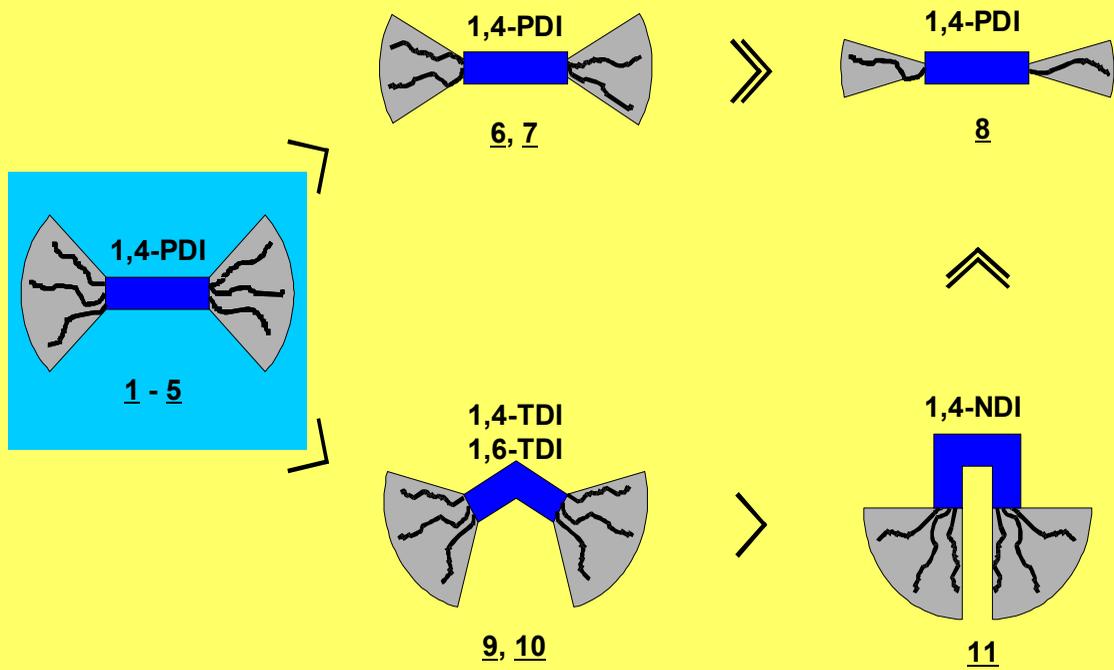
Realized with Bis[(alkoxy)benzoyl]semicarbazides



$R_i = H, C_nH_{2n+1}O-$ ($n = 6, 8, 10, 12, 14, 16$), $CH_2=CH-(CH_2)_9O-$

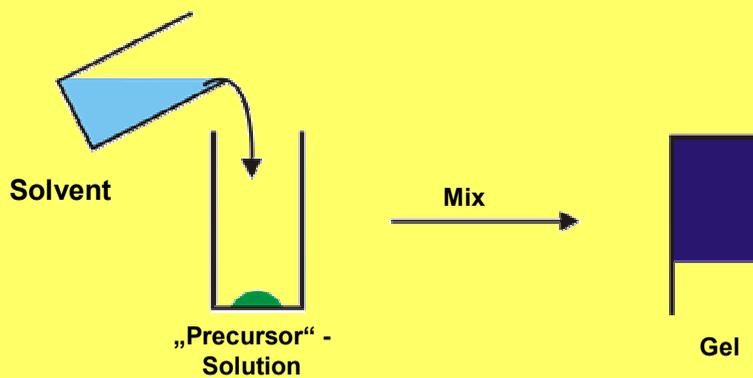


Gelation and Molecular Geometry





2) „Cold Gelation“

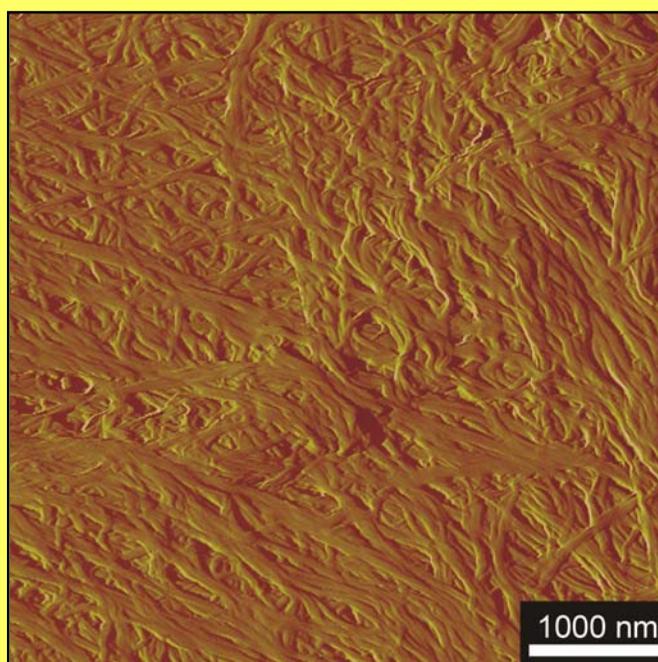
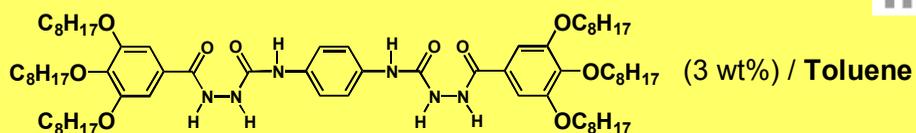


- + rapid method, defined starting point
- + no thermal load of the liquid to be gelled
- + „Liquid“ + „Liquid“ \longrightarrow Gel
- „Precursor“-Solvent in Gel

Table 3: Gelation of toluene, chloroform, n-hexane, and 1,3,5-tri(isopropyl)benzene by mixing with precursor solutions of bis(semicarbazides) (T = 20 °C)

No.	precursor solvent	[No.] ₀ /wt%	solvent added	[PS] _f /wt%	[No] _f /wt%	[Nr] _f mol/L	observation at 10 min	15 h
4	DMF	16,7	toluene	7,6	1,5	0,015	GT	GT
4	DMF	33,3	toluene	3,2	1,5	0,015	GC	GT
4	DMF	44,4	toluene	1,4	0,8	0,008	Sv	GC
4	DMF	3,9	toluene	1,9	1,3	0,013	GC	GC
4	DMF	33,3	chloroform	3,2	3,2	0,032	GT(i)	GO
4	DMF	33,3	chloroform	1,6	1,6	0,016	Ssv(i)	GT
4	DMF	33,3	chloroform	0,8	0,8	0,008	Sv(i)	GO
4	DMF	33,3	chloroform	0,4	0,4	0,004	Sv(i)	GT
2	DMA	20,0	toluene	10	2,5	0,021	GT	Sv
2	DMA	33,3	toluene	5,0	2,5	0,021	GT	GT
2	DMA	33,3	toluene	1,7	0,8	0,007	GC	GC
2	DMA	33,3	n-hexane	6,2	3,1	0,026	GC	GC
2	DMA	33,3	n-hexane	2,2	1,1	0,009	GC	GC
2	DMA	33,3	TPB	3,0	1,4	0,012	GC	GC
2	DMA	33,3	TPB	1,5	0,7	0,006	GC	GC
2	DMA	33,3	TPB	0,8	0,5	0,004	GC	GC
2	DMA	33,3	TPB	0,4	0,25	0,002	Ssv	GC
2	DMA	33,3	TPB	0,2	0,12	0,001	Sv	Ssv

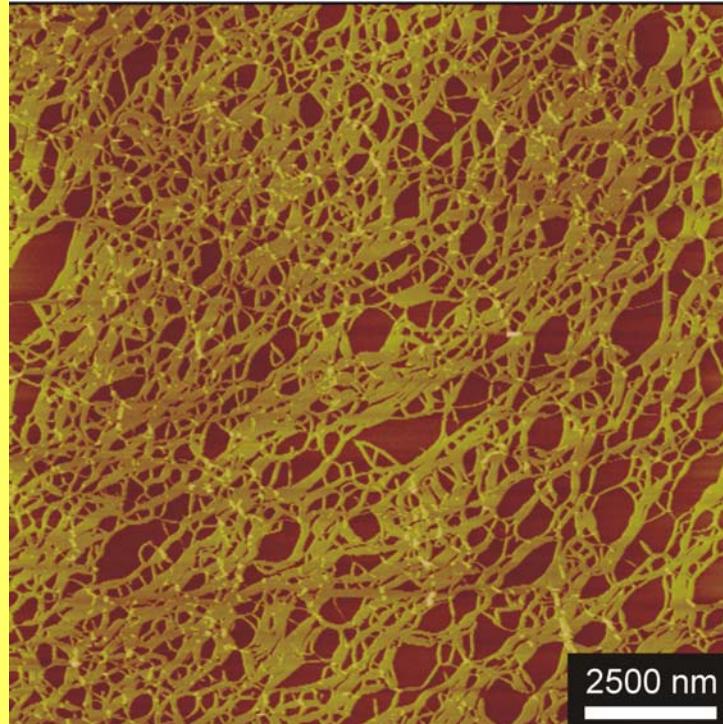
[Nr]₀ = concentration of the semicarbazide in the precursor solution, [PS]_f = concentration of the precursor solvent in the final mixture, [Nr]_f = concentration of the semicarbazide in the final mixture, DMF = dimethylformamide, DMA = dimethylacetamide, TPB = 1,3,5-tri(isopropyl)benzene, GO = opaque / white gel, GT = translucent / turbid gel, GC = clear gel, P = precipitate, S = clear solution, Sv = clear, viscous solution



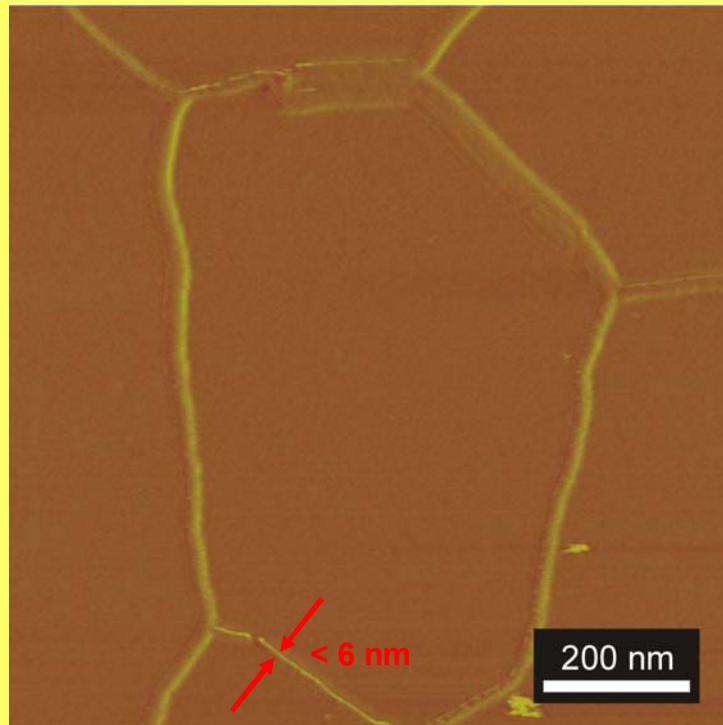
Dried Gel:

$$\varnothing_{\text{Faser}} = 150 \pm 30 \text{ nm}$$

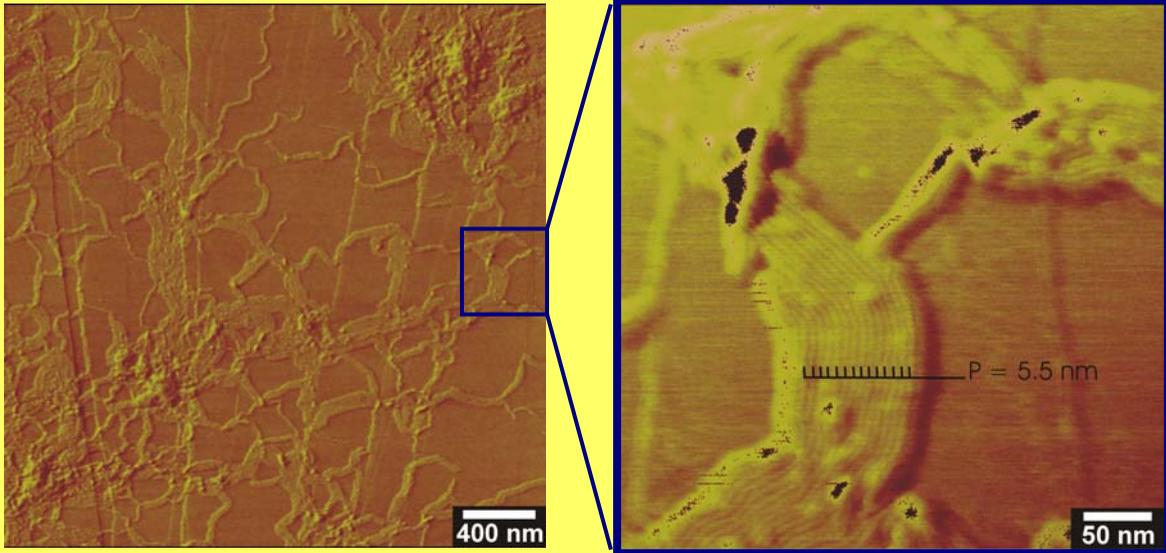
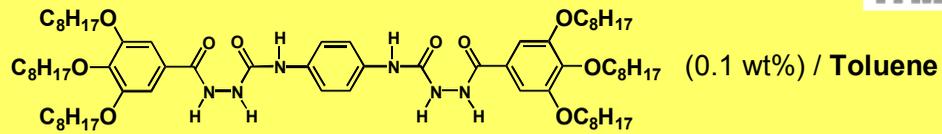
AFM – Scan,
Tapping-Mode,
Amplitude – Signal



Dried **DBSC-8** Gel (0,25 wt% in toluene, diluted to **0,012 wt%**, Spin Coat on Mica, 2000 rpm)

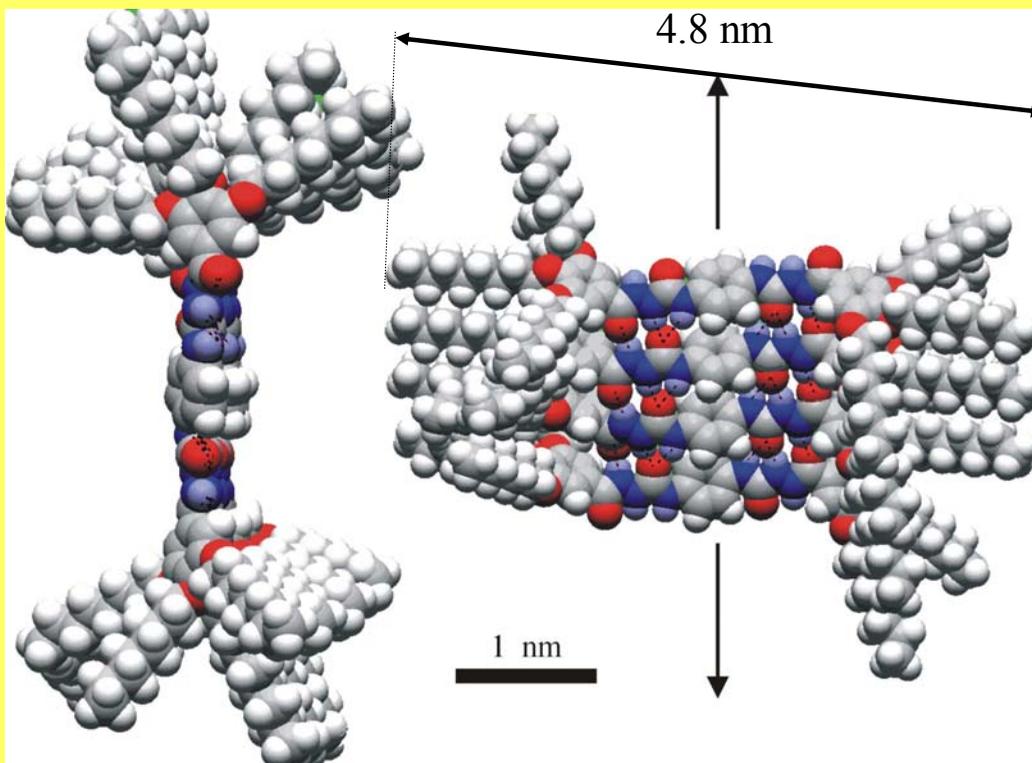


Dried **DBSC-8** Gel (0,25 wt% in toluene, diluted to **0,002 wt%**, Spin Coat on Mica, 2000 rpm)

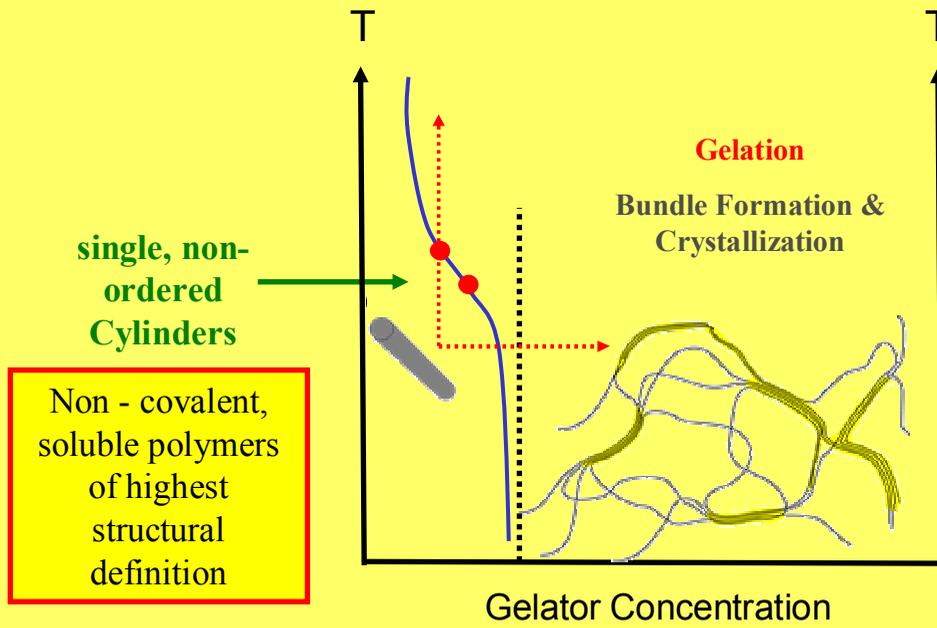


Dried **DBSC-8** gel (0,10 wt% in toluene, Spin Coat on HOP graphite , 2000 rpm)

Tapping Mode SFM, Phase Signal

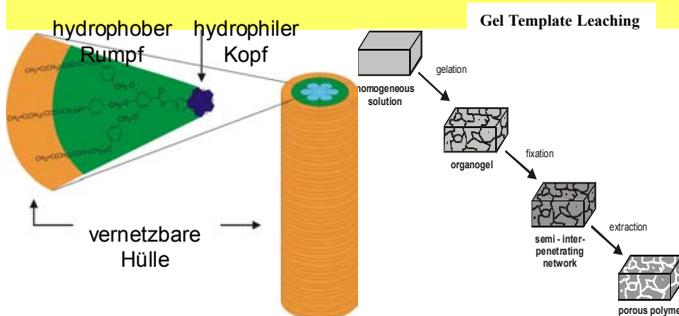


Macromodel 7.0, MMFF – Force-Field



Aim: Control of Bundle Formation *via* the Structure of the Gelator

Formation of Discrete Cylinders in Thermodynamic Equilibrium



Mineralisation

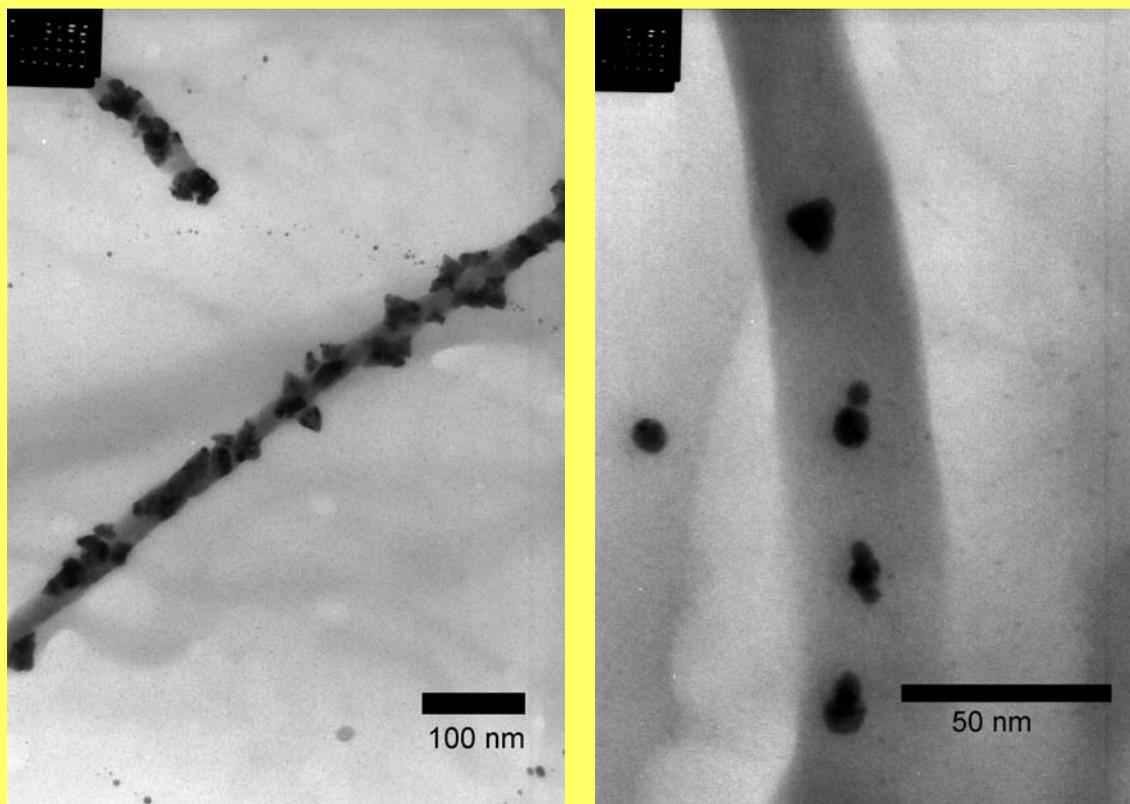
Supramolecular Organogels

New Polymers, Macromolecules

Adaptive Systems

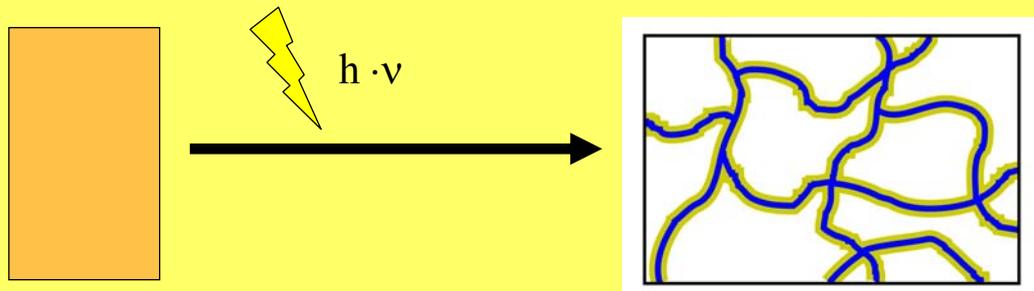
Mineralization of Gold – Nanoparticles in Bis[(alkoxy)benzoyl]semicarbazid - Organogels

U. Beginn, A. Koch

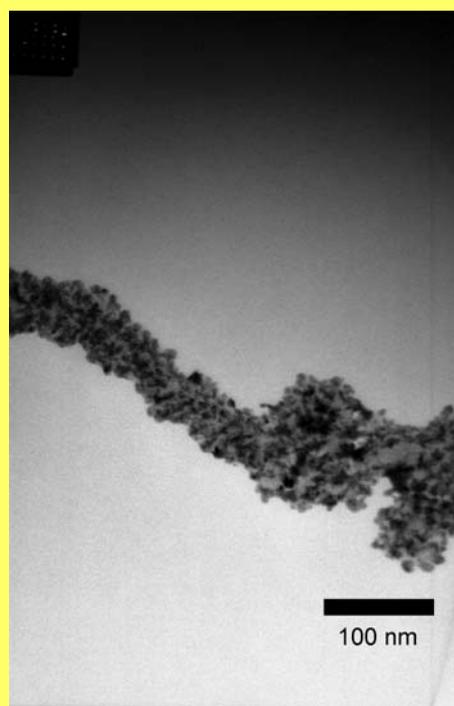
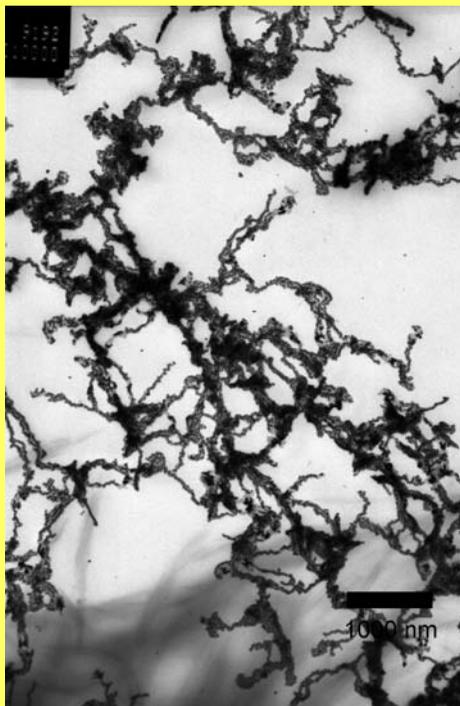


U-Rohr: 16 wt% $[N(Oc)_4][AuCl_4]$ in Toluene / 2 wt% DBSC8 in Toluene* / Hydrochinone in THF sat.

* Mother solution: 33 wt% DBSC8 in DMAc / gel annealed for 5 min at 100°C.

Photochemical Reduction:

**Gold - loaded
Organogel**

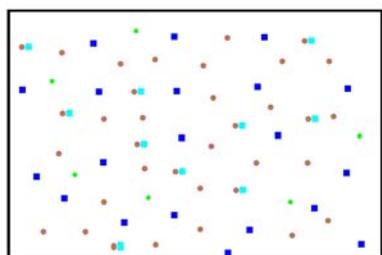


DBSC6 (5wt%) + $[N(Oc)_4][AuCl_4]$ (2 wt%) in Toluol

20 h (= 2 x 10h) Illumination in Sunlight: transparent, red Gel

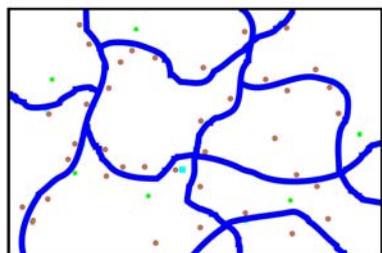
Mineralisation in Organogels

①



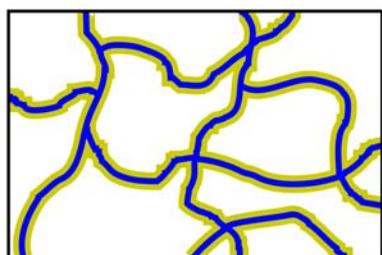
Homogeneous Solution from
 (a) Organogelator (■),
 [(b) *Metal-binding Gelator* (●■),]
 (c) Metal-Precursor (●) and
 (d) Reduction agent (◆).

②



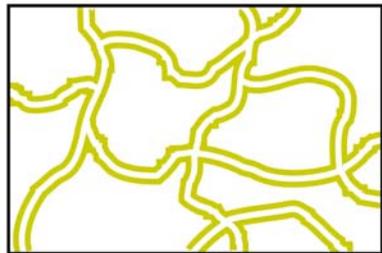
Organogel containing metal -
 adsorbing Sites

③

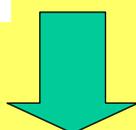


Reduction of the metal -
 precursor
 Formation of a metal - layer
 on the gel fibres

④



Heat treatment:
 drying, 'calzination', sintering



Mesoporous Metal Network

Properties of mesoporous metal networks:

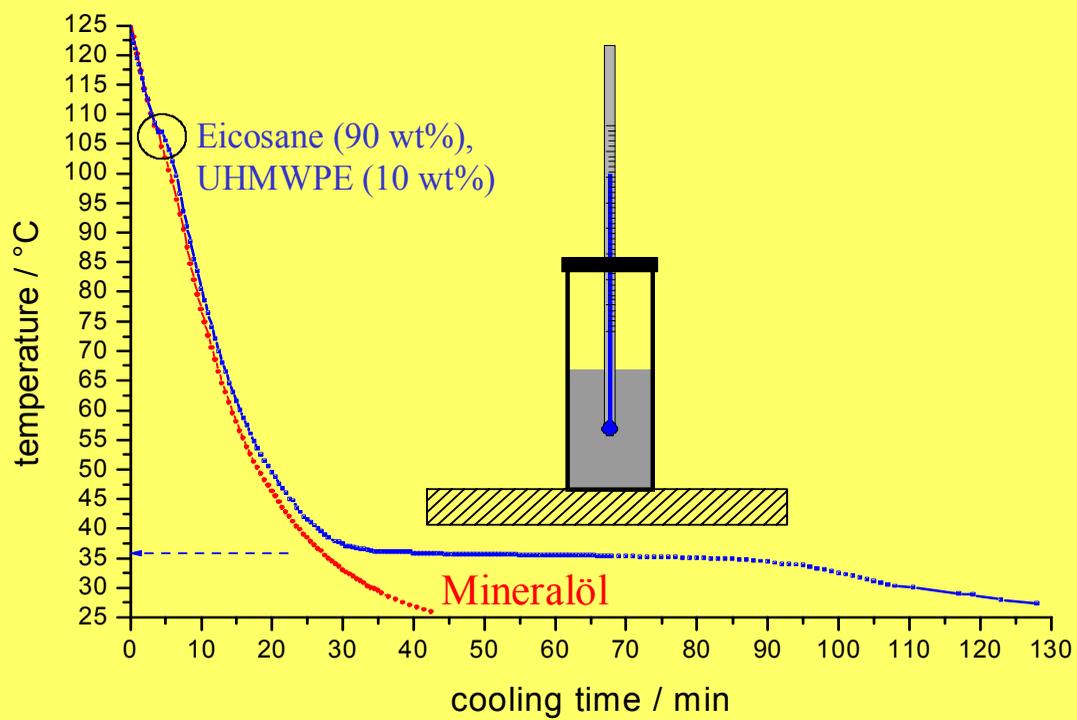
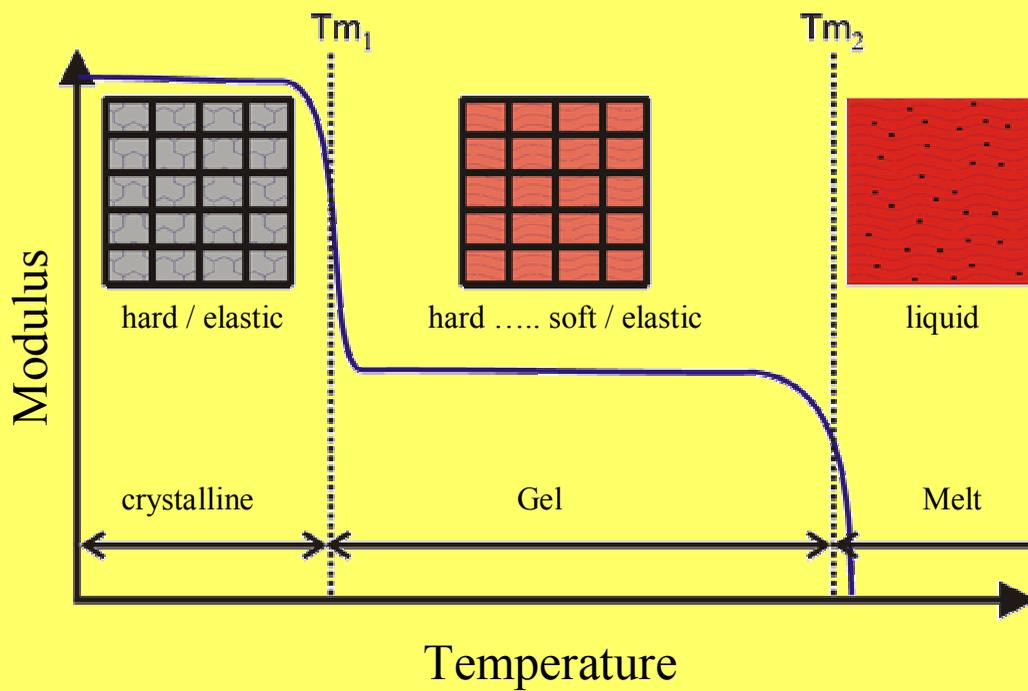
- a) Large inner surfaces ($> 100 \text{ m}^2/\text{cm}^3$)
- b) Electrical conductivity
- c) (Catalytic activity)

Possible Applications:

- Elektrodes for electro chemistry
- Catalysts
- Conductive Coatings

Adaptive Materials –**„PCM's“****U. Beginn**

Phase Change Materials



Thank you...

Bernd Tartsch

Linglong Yan

Yvonne Noppeney

Marat Galliamov

Prof. S. Maghonov

Dr. K. Haubennestel

Dr. Xiaomin Zhu

Prof. Martin Möller

Grants

DGF (SFB 569 – A6), Universitätsgesellschaft Ulm, Land
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