

Chirality in Physical Gels

OUTLINE

What is a gel?

What is a molecular gel?

Structures at different length scales and flow characteristics.

Examples and applications of polymer gels—2D self-assembly.

Examples and applications of molecular gels—3D self-assembly.

Chirality in Self-Assembled Fibrillar Networks (SAFINs) of gels

Sergeants and soldiers

Structures

Role of solvent

Other properties

“MOLECULAR GELS. Materials with Self-Assembled Fibrillar Networks”, Richard G. Weiss and Pierre Terech, Eds., Springer, 2005.

Where are gels??

Our bodies

Jelly fish

Microbiology—actin, clathrin, tubulin,
amyloids (Alzheimer's disease)

Pharmaceutical delivery agents—vitamin E

Tooth paste, deodorants, cosmetics, soap

Food—Jell-O, gummy bears, aspic

Slime

Industrial products—paints, inks, adhesives,
soles in athletic shoes

GPC and gel electrophoresis

Early photography

What are gels??

“While the rigidity of the crystalline structure shuts out external expressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself.....The colloid possesses **ENERGIA. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality.”**

Thomas Graham, *Phil. Trans. Roy. Soc.* **1861**, 151, 183.



Master of the Mint

“The colloid condition, the “gel,” is one which is easier to recognize than to define.”

Dorothy Jordan Lloyd In *Colloid Chemistry*; Alexander, J., Ed.; The Chemical Catalog Co.; New York, 1926; Vol. 1, p 767.

“Gels are infinitely viscous slime.” **RGW**, *unpublished forever*.

MOLECULAR GELS ARE:

SELF-ASSEMBLED FIBRILLAR NETWORKS
(**SAFIN**s)

OF LOW MOLECULAR-MASS ORGANIC
GELATORS (**LMOG**s)

ENTRAPPING PHYSICALLY A LARGE VOLUME
FRACTION OF LIQUID WHOSE

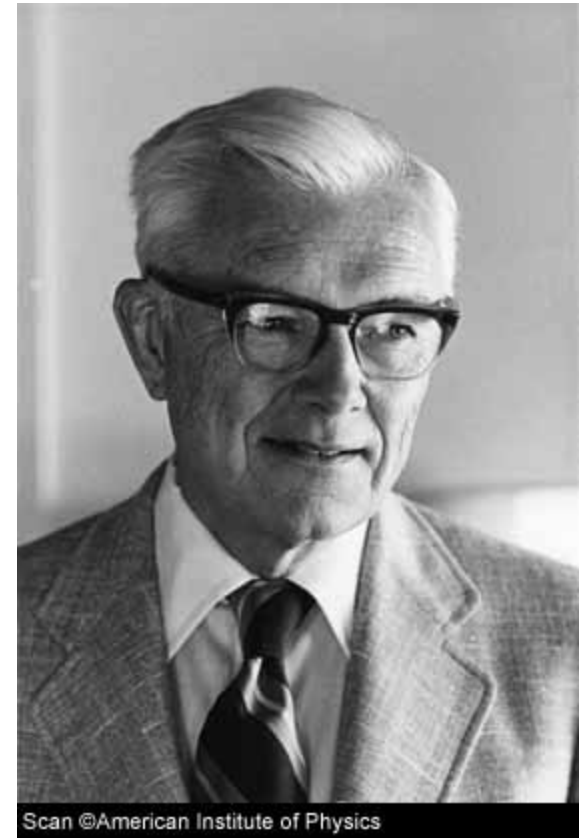
RATE OF SHEAR NOT PROPORTIONAL TO THE
SHEARING STRESS (*non-Newtonian liquid*).

They form above a saturation limit of the LMOG.

SUPRAMOLECULAR SELF-ASSEMBLY
OR CRYSTALLIZATION GONE AWRY??

Paul Flory's four classes of gels

1. Well-ordered lamellar structures.
2. Cross-linked polymeric networks swollen with solvent; disordered polymer chains.
3. Polymer networks in which the chain-chain interactions are physical.
4. Particulate disordered structures...such as *molecular gels*.



The story of Jell-O

In 1897, Pearle B. Wait, a carpenter in LeRoy, NY, was putting up a cough remedy and laxative tea in his home. He experimented with gelatin and came up with a fruit flavored dessert which his wife, May, named Jell-O. (www.jellomuseum.com)



Pearle B. Wait



What is Jell-O?

Water

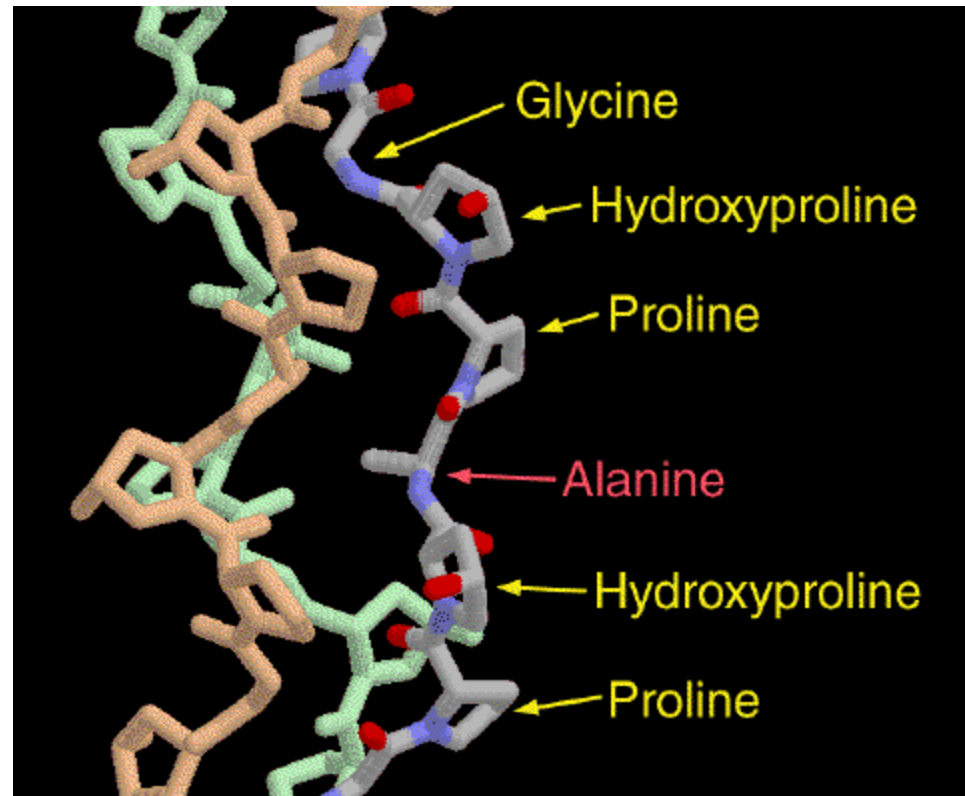
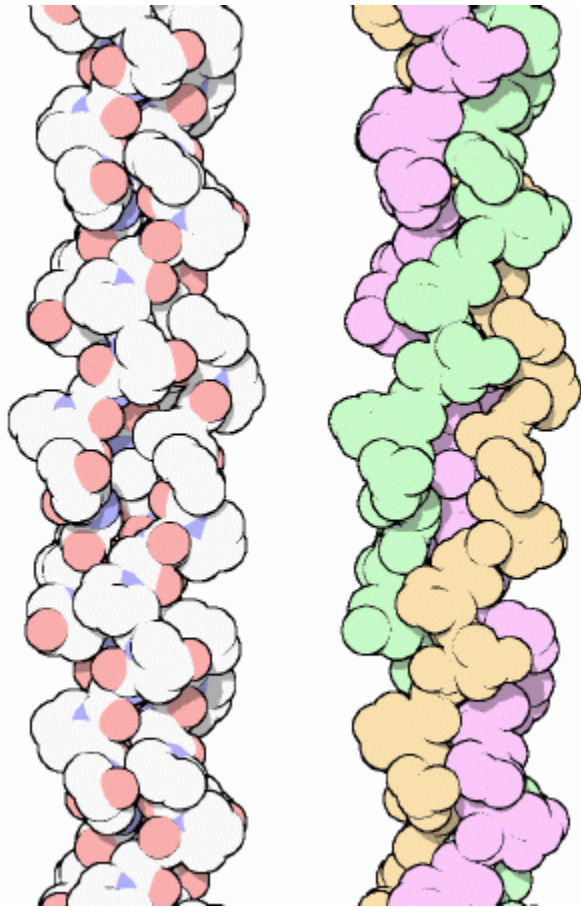
Denatured collagen (or agar-agar)

Sugar

Flavorings

Artificial coloring

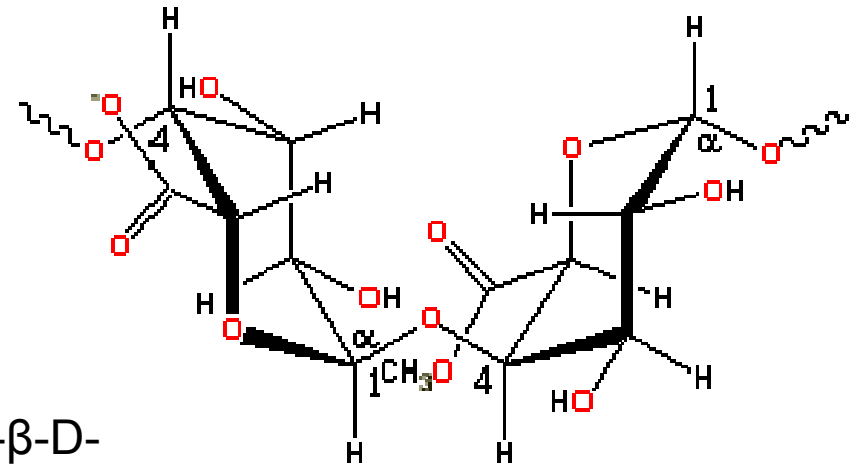
Collagen—our most abundant protein and a hydrogelator



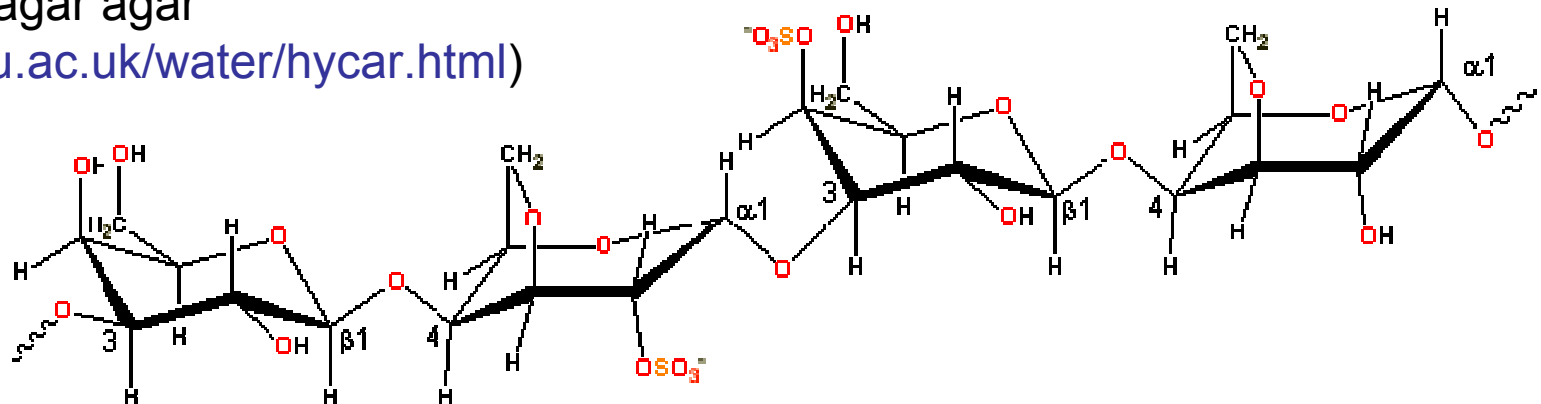
When heated, the triple helix of collagen unwinds and the chains separate. When it cools down, the denatured structure takes in water, forming gelatin (www.rcsb.org/pdb/molecules/pdb4_3.html).

Polysaccharide hydrogelators

Pectin—mostly homopolymeric partially methylated poly- α -(1 $\rightarrow$ 4)-D-galacturonic acid residues in fruits (www.lsbu.ac.uk/water/hypec.html)



Carrageenan—mainly alternating 3-linked- β -D-galactopyranose and 4-linked- α -D-galactopyranose units polysaccharides prepared by alkaline extraction (and modification) from red seaweed (*Rhodophyceae*); thermoreversible hydrogels in presence of appropriate counterions; like agar agar (www.lsbu.ac.uk/water/hycar.html)



Aluminum soaps for gelling hydrocarbons

Treatment of Wells

Joseph B. Clark, Standard Oil and Gas Company, Tulsa, OK

For oil well 'fracturing':

"introducing.....a low viscosity hydrocarbon liquid and a hydroxy aluminum soap gel-forming material..."

(US Patent 2,596,844, May 13, 1952)



Louis F. Fieser, George C. Harris¹, E. B. Hershberg², Morley Morgana³,
Frederick C. Novello⁴, and Stearns T. Putnam⁵

GIBBS LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE, MASS.

Ind. Eng. Chem. **1946**, 38, 768

The first use of a fuel line fuel thrower in the development of acids of the types exemplified by lauric acid and by naphthenic or oleic acid. A description is given of early work on the problem conducted under the National Defense Research Committee in cooperation with Edgewood Arsenal. Photo above shows operation of a portable flame thrower utilizing Napalm fuel (reproduced through courtesy of Standard Oil Development Company).

IN MILITARY idiom the name Napalm has been used to designate either a special aluminum soap employed by Chemical Warfare Service as a thickening agent, a gasoline gel produced with this agent and used as a flame thrower fuel and for filling the M-49 and M-47 bombs and other incendiary munitions, or even a Napalm gel-filled incendiary itself: "One Napalm (fire bomb) on target. . . ." In this paper an account will be given of early work conducted at the Gibbs Laboratory in cooperation with the Chemical Warfare Service group at Edgewood Arsenal, Md., on the development of Napalm-type gelling agents. The subsequent work on the manufacture, standardization, and stabilization of the eventual product was carried to a successful conclusion through the combined efforts of Chemical Warfare Service laboratories, manufacturers, and NDRC groups other than our own; this report will describe merely the initial research conducted in 1941-42.

The background for the research was provided by an interesting series of circumstances starting, in the summer of 1941, with

¹ Present address, Hercules Powder Company, Wilmington, Del.

² Present address, Schering Corporation, Kenilworth, N. J.

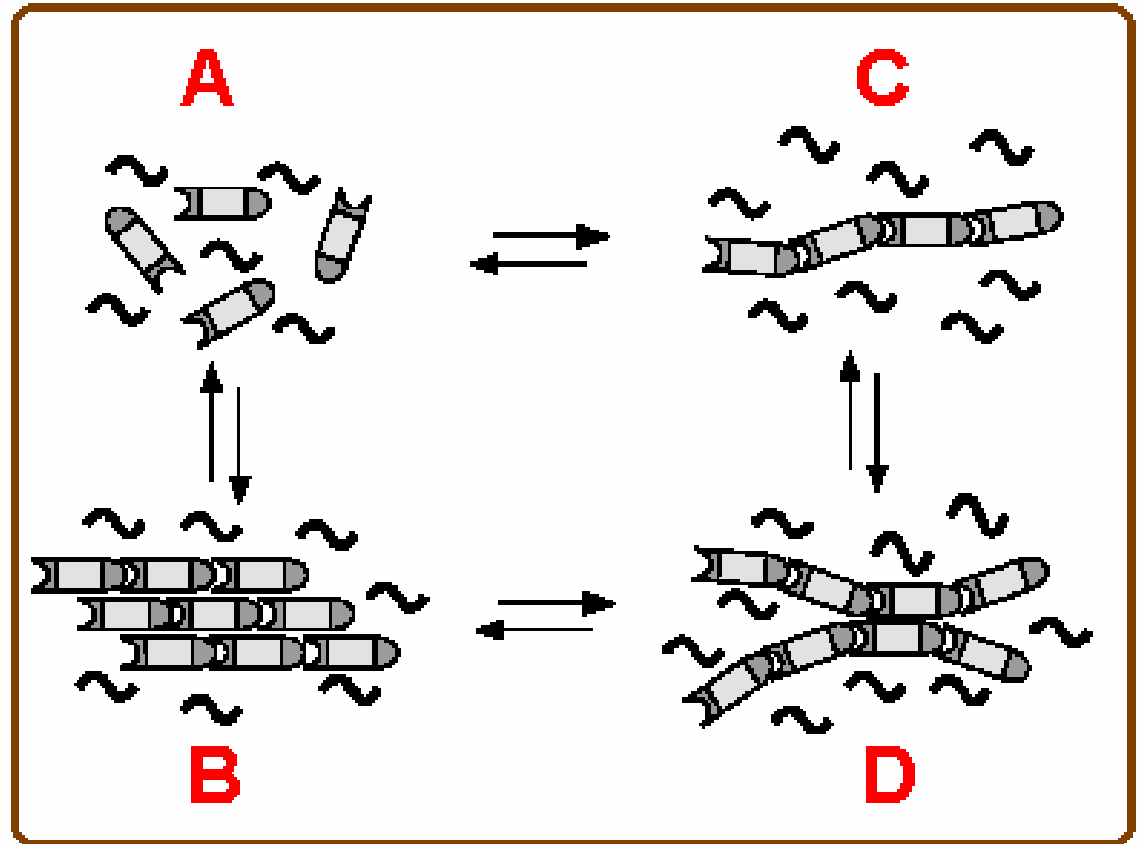
³ Present address, Eshel Corporation, Detroit, Mich.

⁴ Present address, Sharp and Doherty, Inc., Glenolden, Pa.

structural character were without avail. We observed, however, that when either divinylacetylene or the commercial polymer known as Synthetic Drying Oil was shaken with oxygen, transformation occurred to a peroxide-containing sticky gel. When ignited with a match, this gel burned with a sputtering, spectacular flame, and trials in simulated explosion- or scatter-type bombs convinced us of the potential value of a gelled hydrocarbon fuel that would be distributed over a target area in the form of burning, adherent masses. Major Gerrard Rambaut, of the British Air Ministry, encouraged the continuation of work on incendiary gels; he told of the parallel development of rubber-benzene gels in England and advised that some test be worked out for evaluating incendiary materials. A method that proved to be a useful guide was soon introduced and eventually refined: A standard volume of gel dispensed from a modified grease gun was burned in a draft-free room on a wooden structure consisting of a base-board provided with four 2 x 4 inch uprights connected by crossbeams, and the results were expressed in terms of the weight of wood destroyed and the burning time. Such burning tests soon provided evidence that the gels from divinylacetylene, even when fortified with chlorates or nitrates, were more spectacular than effective. Rubber gels proved to be better; consequently, extensive studies were made in the fall and winter of 1941 on the preparation and incendiary properties of 6-8% gels of smoked sheet, crepe, and latex rubber in gasolines, naphthas, and other less available hydrocarbon fuels. During this period bombing tests conducted at Edgewood Arsenal established the penetrability of employing a rubber-gasoline gel as a filling for the available M-47 100-pound bomb. Then came Pearl Harbor and the sudden cancellation of rubber from the list of available stores. In response

Back to molecular gels

- ❖ thermoreversible
- ❖ quasi-solid
- ❖ composed of a liquid and a low concentration of an **LMOG**
- ❖ return to their original form when relieved of an applied stress (below a stress limit)
- ❖ cross-linked network



Adapted from: Schoonbeek, PhD Thesis, Univ. Groningen, The Netherlands, 2001.

Must be defined at different length scales—from **macroscopic** to **nanometric**—and according to responses under stress

A case study of morphology: from the macroscopic to the molecular

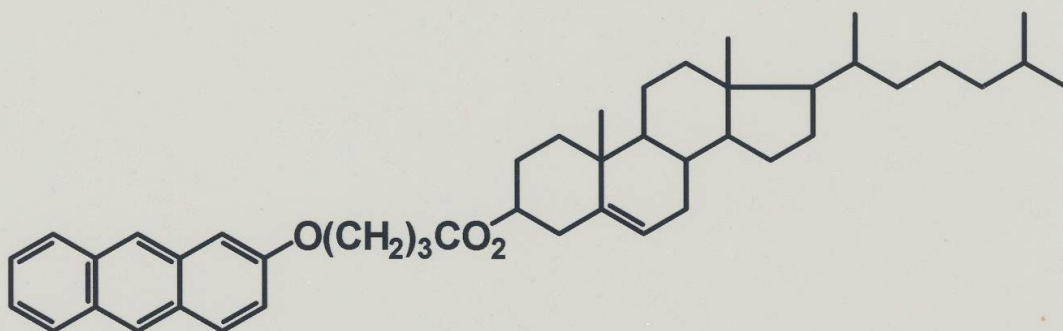
1.3 wt% CAB/benzene (isotropic phase)



1.2 wt% CAB/*n*-dodecane (gel phase) under black light



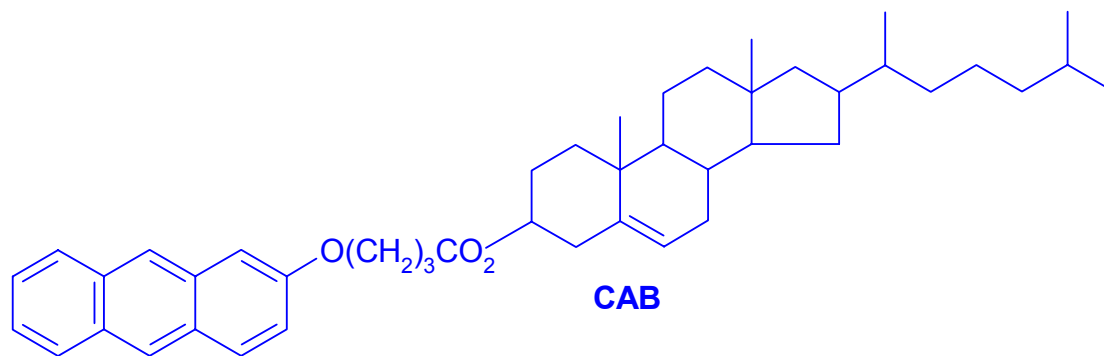
1.2 wt% CAB/*n*-dodecane (gel phase) inverted



CAB

Lin, Weiss,
Macromolecules 1987, 20,
414.

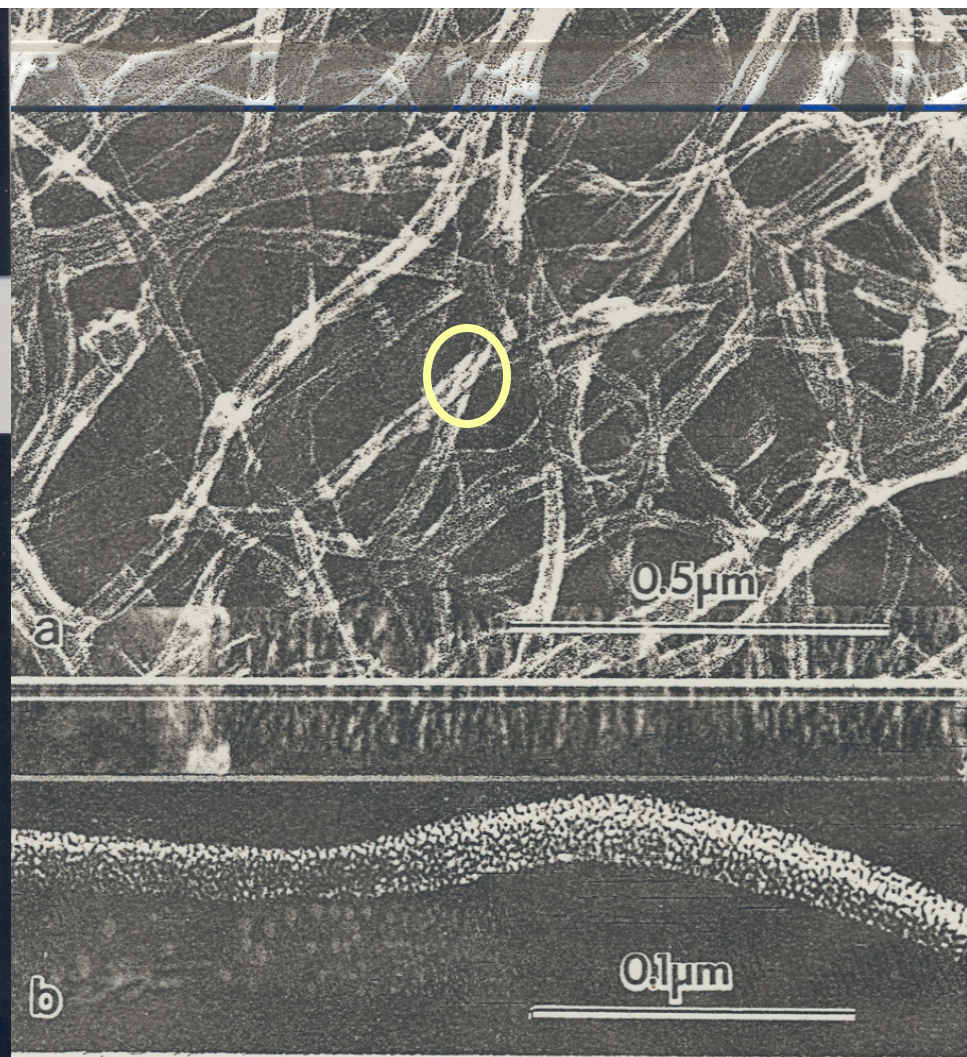
Lin, Kachar, Weiss, *J. Am. Chem. Soc.* 1989, 111,
5542.

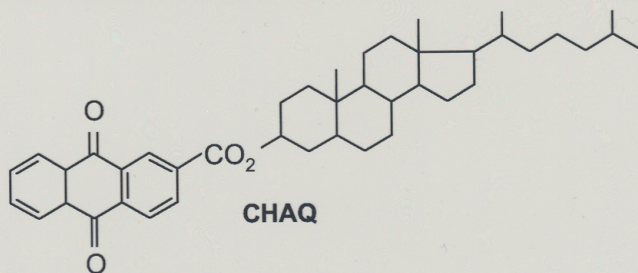
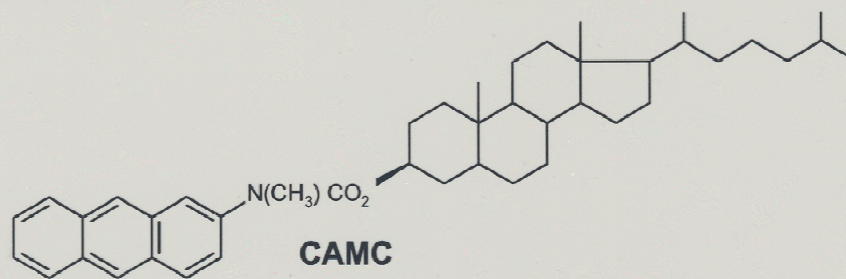
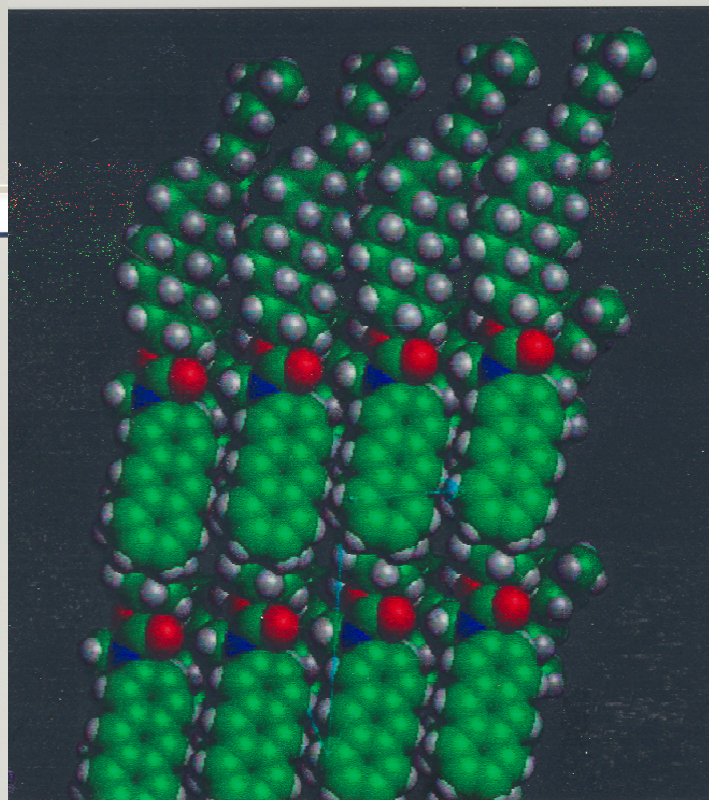
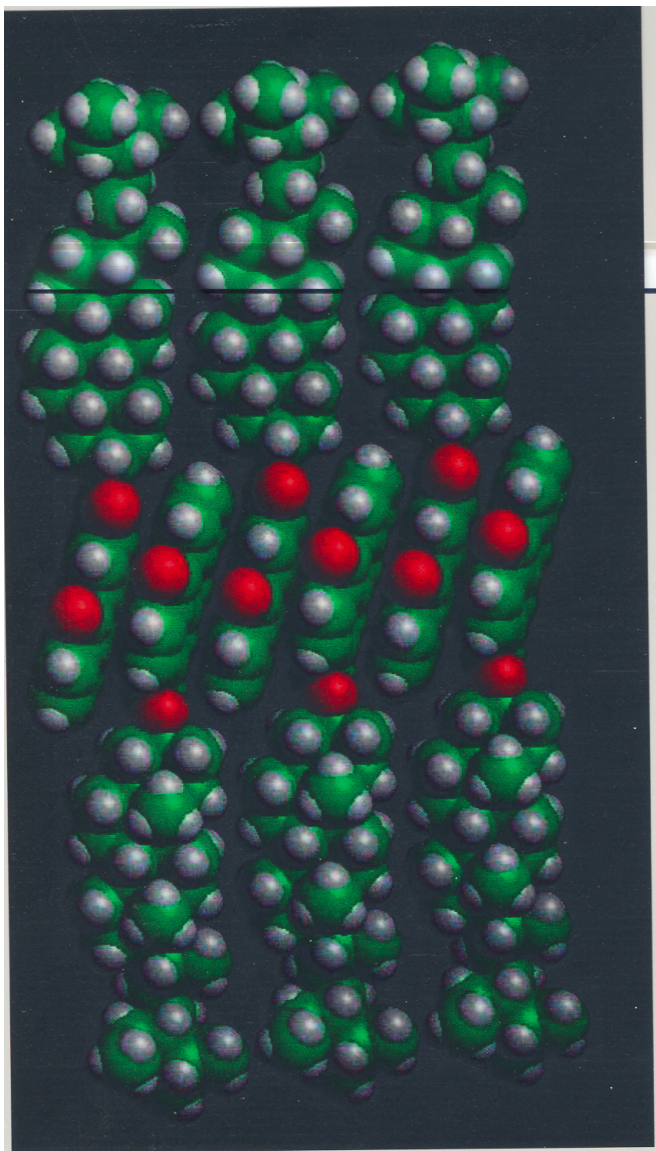


0.80 wt%

CAB in *n*-dodecane

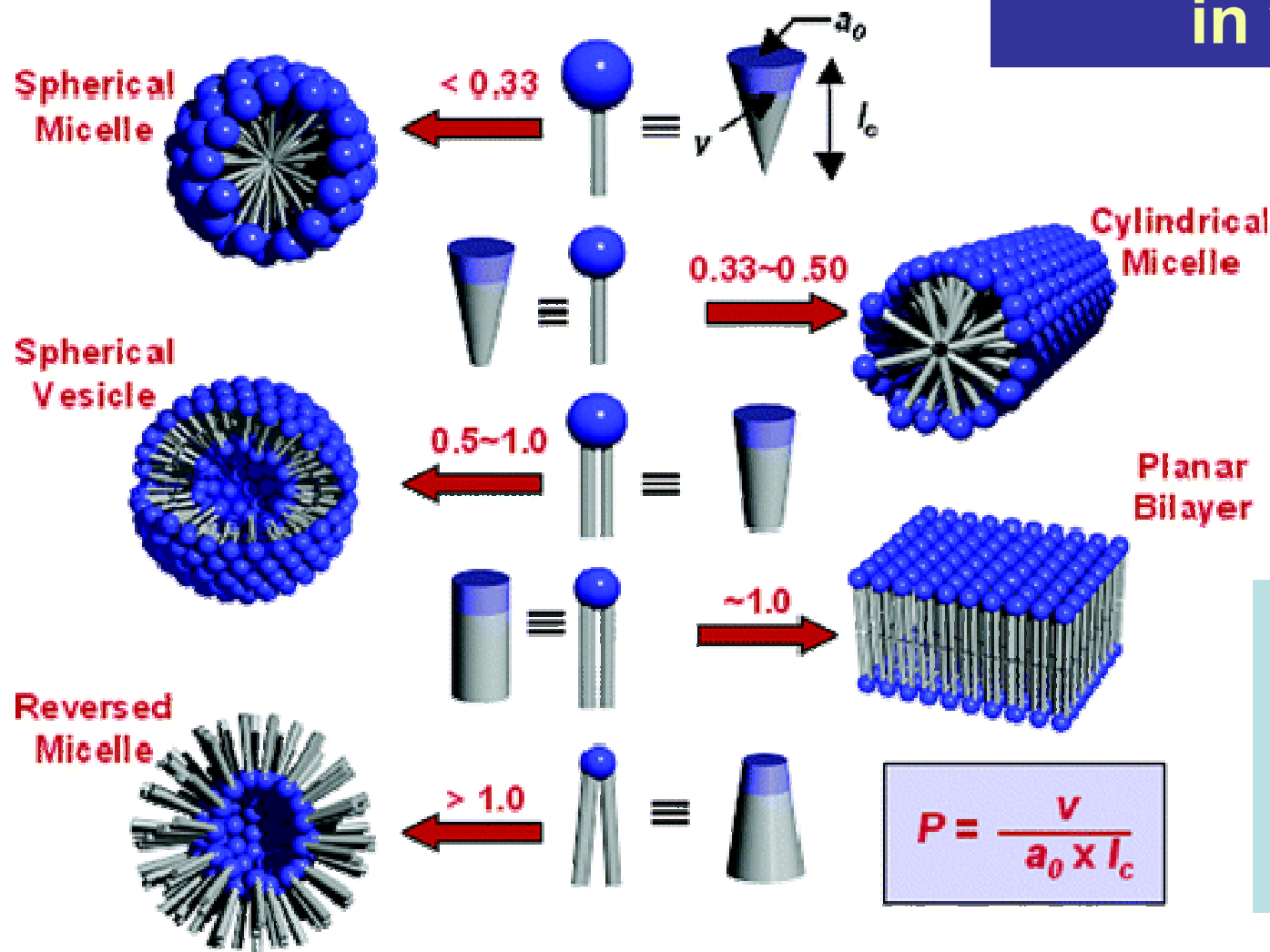
2.2 wt%





Lu, Cocker, Bachman, Weiss
Langmuir, **2000**, 16, 20.
 Mukkamala, Weiss, *Langmuir* **1996**,
 12, 1474.

Self-assembled morphologies of lipids *with liquid chains*: Israelachvili critical packing parameter (P) in water

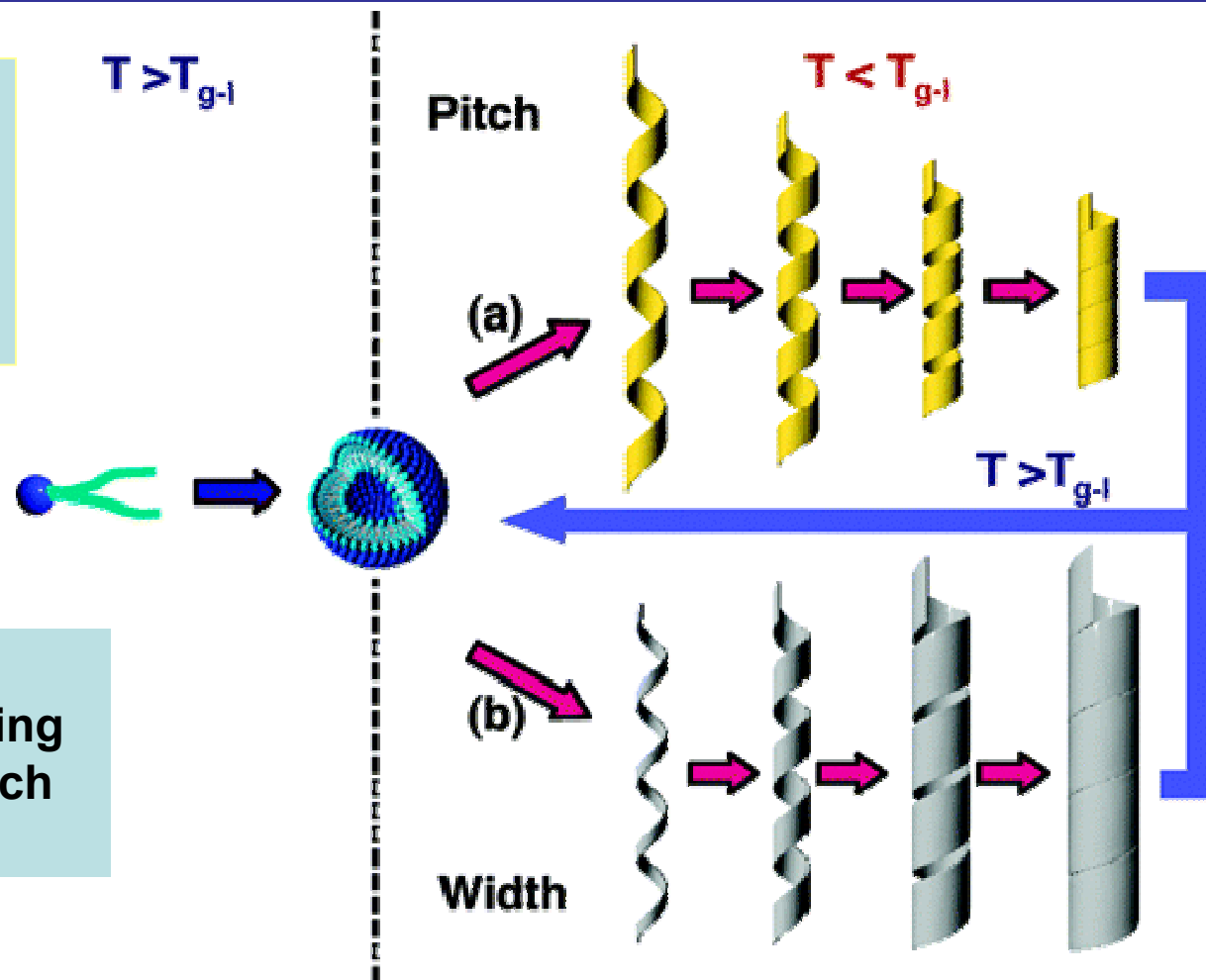


Israelachvili, *Intermolecular and Surface Forces*; Academic Press: New York, 1985. Shimizu, Masuda, Minamikawa *Chem. Rev.* 2005, 105, 1401.

Two possible formation mechanisms for another lipid self-assembly, chiral nanotubes

shortening of the helical pitch of the ribbon while maintaining a constant tape width

widening of the tape width while maintaining a constant helical pitch (more common)



Shimizu, Masuda, Minamikawa *Chem. Rev.* 2005, 105, 1401.

How to make gels from solutions or sols or to convert gels to solutions or sols

Most common: cooling (to gel) and heating (to make sol)

Other physical methods:

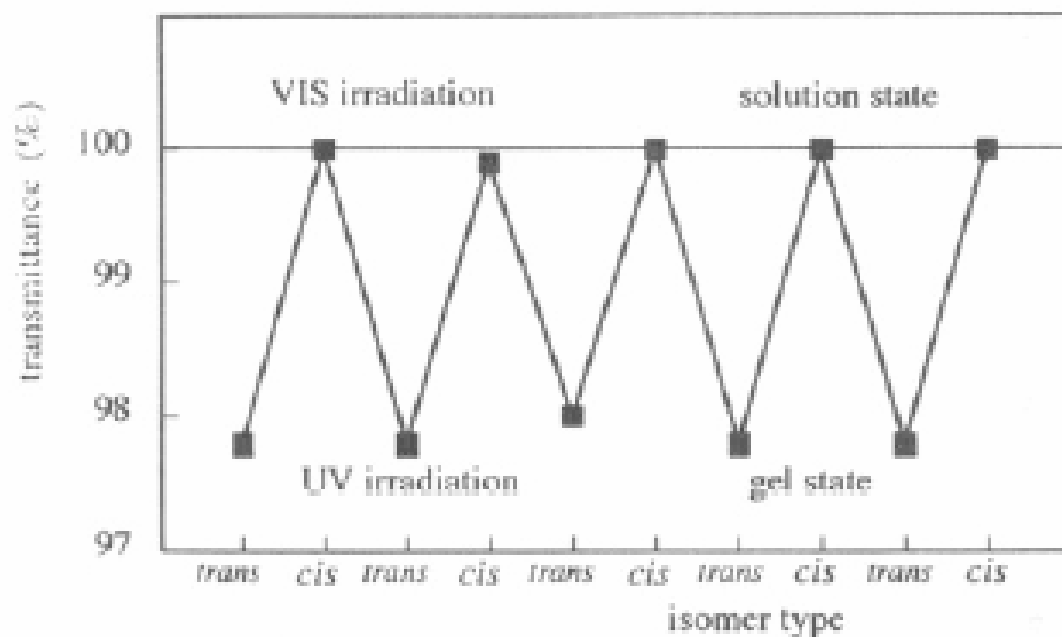
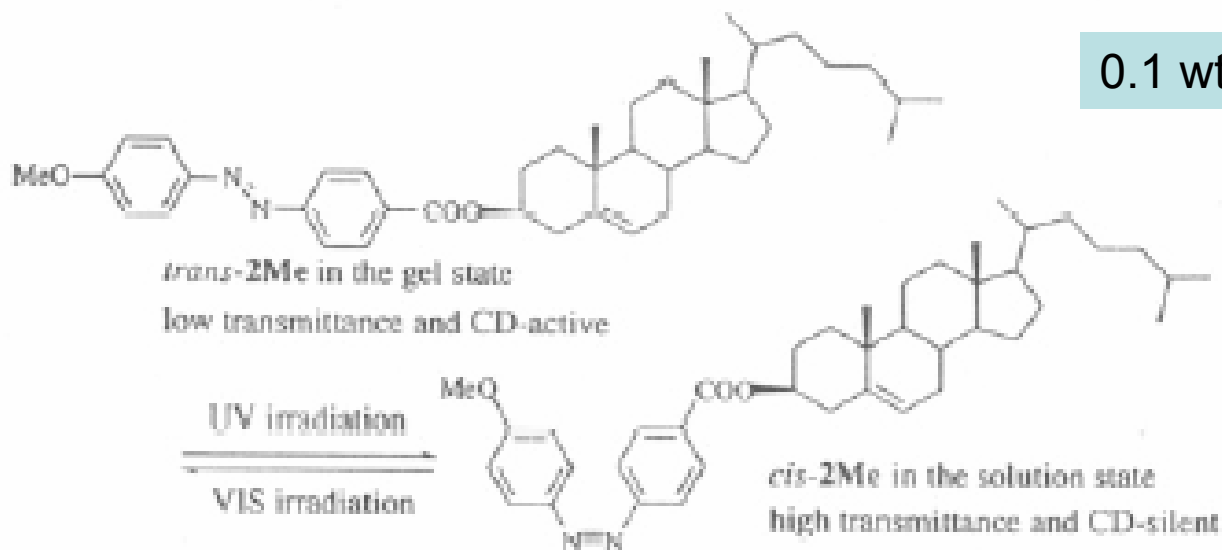
- ❖ mechanical stress (thixotropy)
- ❖ light (photoresponse)
- ❖ ultrasound (aggregation promoted by conformational change)

Chemical methods:

- pH changes
- addition or removal of metal ions
- host-guest complexation
- *in situ* chemical reactions (reversible or irreversible)

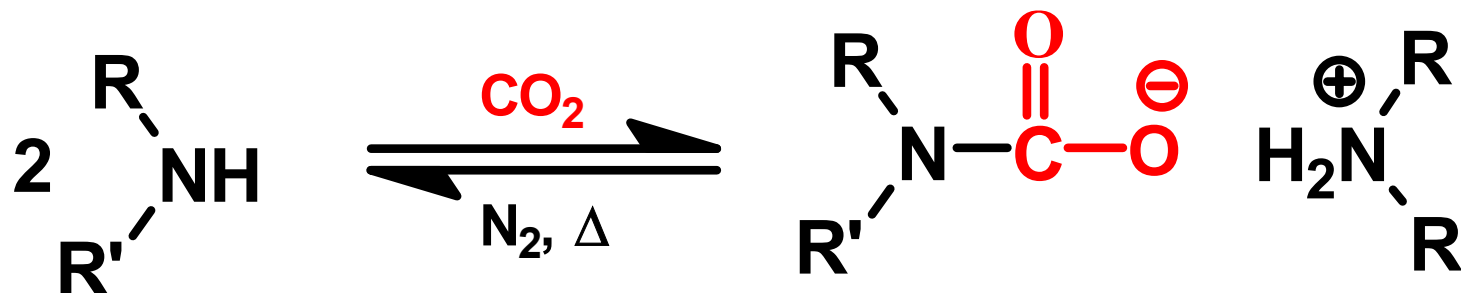
A photochemically reversible example to cycle between gel and sol

0.1 wt% in 1-butanol at 25 °C



Murata, Aoki, Suzuki, Harada, Kawabata, Komori, Ohseto, Ueda, Shinkai *J. Am. Chem. Soc.* 1994, 116, 6664.

Example of reversible thermal reaction to effect gelation: Rheo-reversible gelation by alkylamines and CO₂



	R	R'		R	R'
a	C ₁₀ H ₂₁	H	f	C ₈ H ₁₇	C ₈ H ₁₇
b	C ₁₂ H ₂₅	H	g	C ₁₈ H ₃₇	CH ₃
c	C ₁₄ H ₂₁	H	h	C ₁₈ H ₃₇	C ₁₈ H ₃₇
d	C ₁₆ H ₃₃	H	i	H ₂ NC ₁₂ H ₂₄	H
e	C ₁₈ H ₃₇	H			

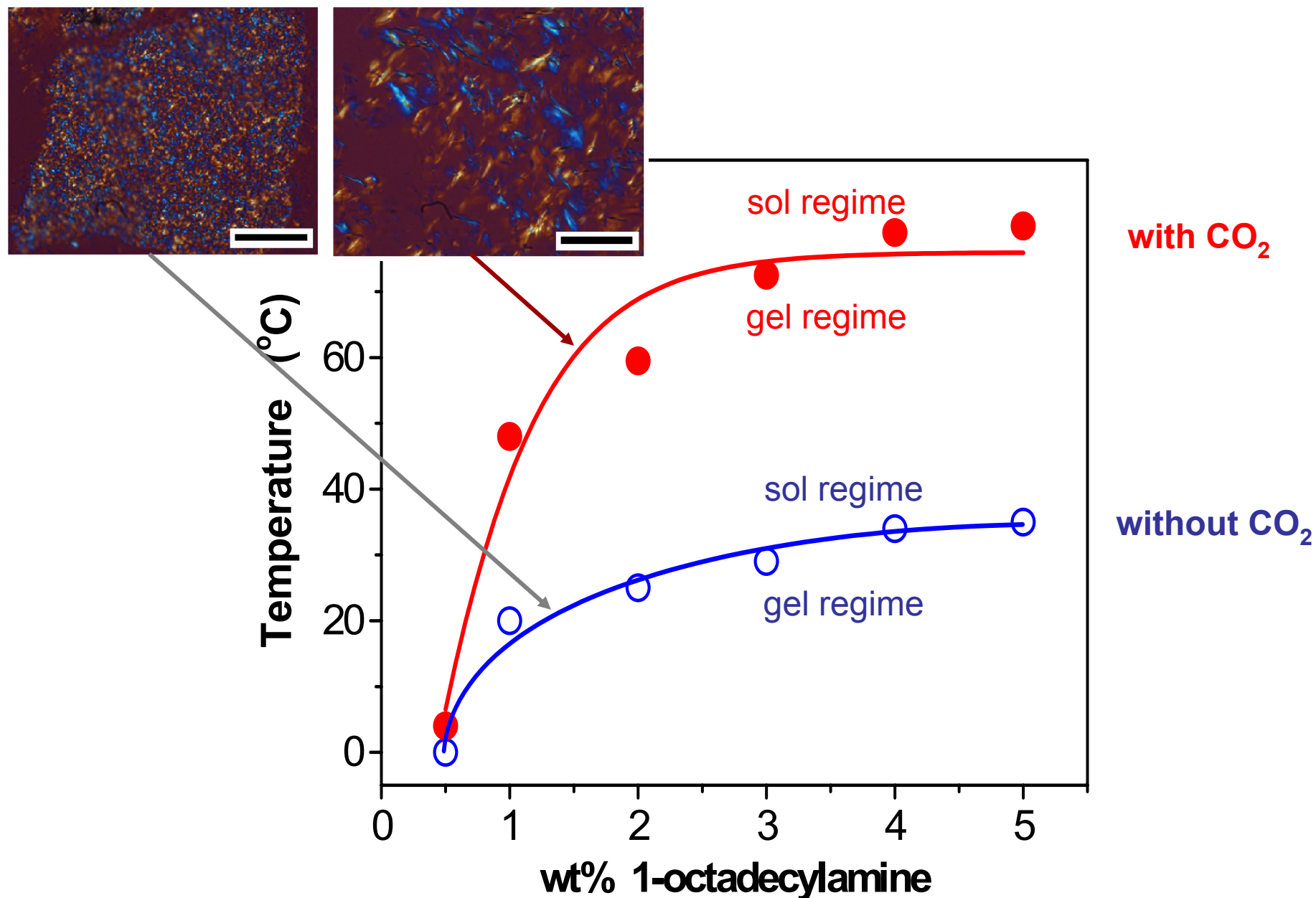
Bannister, Pennance, Curby *US Patent* 3,684,733 (Aug. 15, 1972).
 George, Weiss *J. Am. Chem. Soc.* 2001, 123, 10393.
 George, Weiss *Langmuir* 2002, 18, 7124; *ibid.* 2003, 19, 1017.

5 wt% gels of 1-Octadecylamine

Solvent	Amine (T _g °C)	Carbamate (T _g °C)
Hexane	P	OG (54-56)
n-Octane	P	OG (56-60)
Silicone oil	TG (35)	TG (80)
Ethanol	P	OG (54-56)
1-Butanol	P	OG (49-50)
1-Octanol	P	OG (44-45)
Benzyl alcohol	S	TG (53)
Nitrobenzene	S	TG (<10)
DMSO	TG (53-55)	TG (70-76)
Toluene	S	TG (56)
CCl ₄	P	TG (40-42)

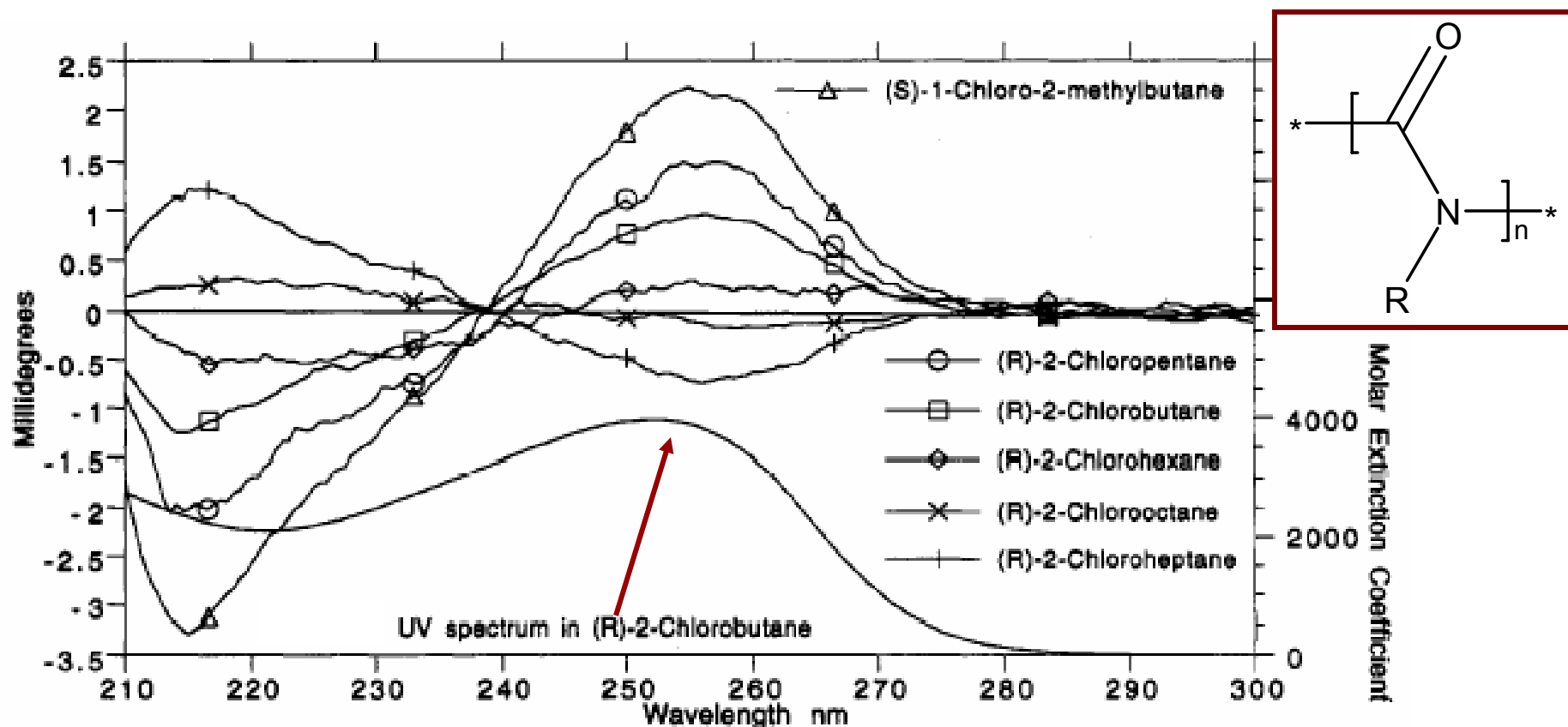
J. Am. Chem. Soc. 2001, 123, 10393

Gelation temperatures in silicone oil for 1-octadecylamine gels



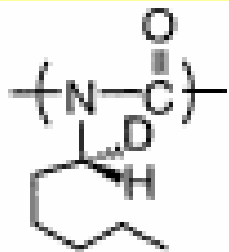
The influence of solvent on fiber shape and twist in Self-Assembled Fibrillar Networks: From molecular to aggregate interactions

Poly(*n*-hexylisocyanate) in optically active solvents at 20 °C



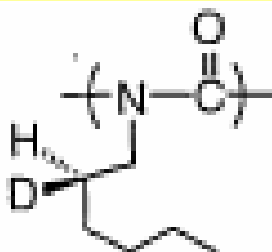
Green, Khatri, Peterson *J. Am. Chem. Soc.* 1993, 115, 4941.

Sergeants and Soldiers: chiral polyisocyanates



$[\alpha]_D -444^\circ$ (*n*-hexane)

$M_v \sim 10^6$



$[\alpha]_D +302^\circ$ (*n*-hexane)

$M_v \sim 10^6$

each separate chiral center contributes 0.36 cal/mol of preference for polymer twisting

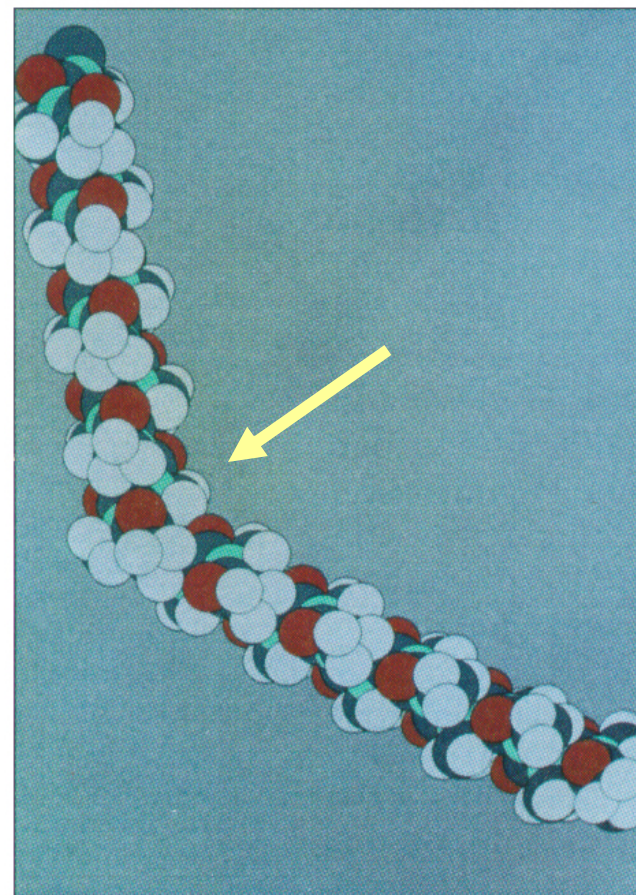
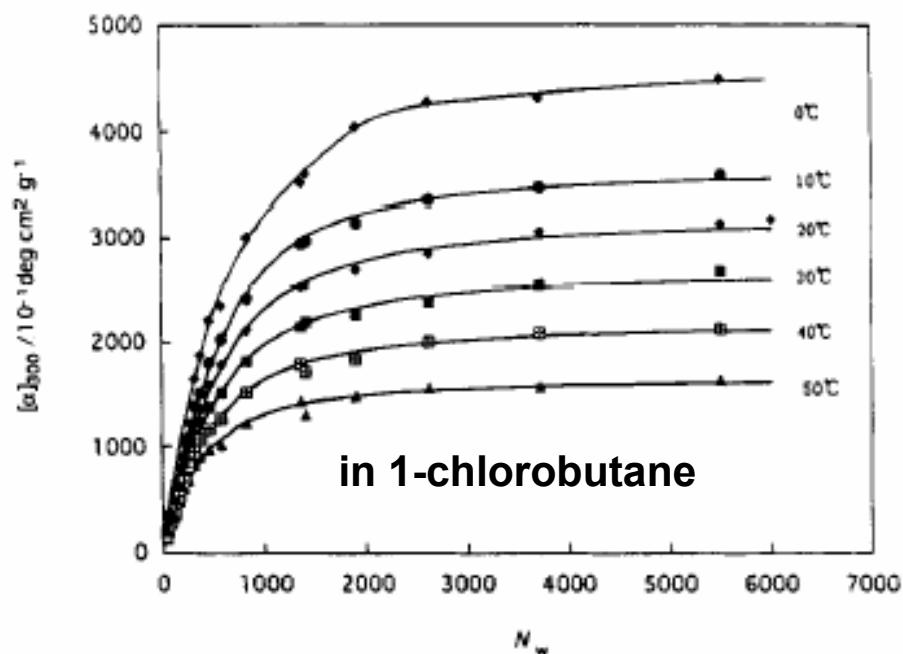
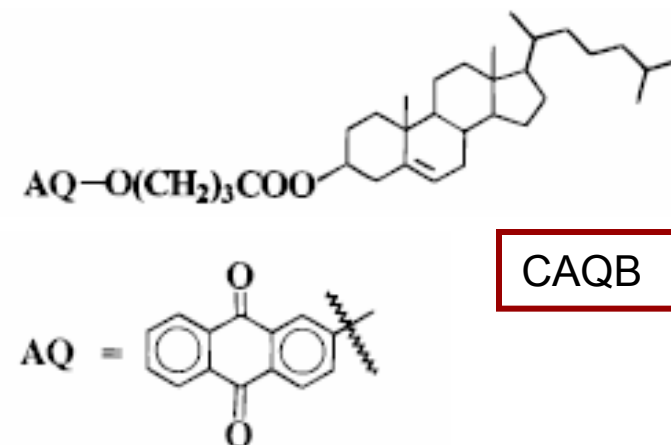
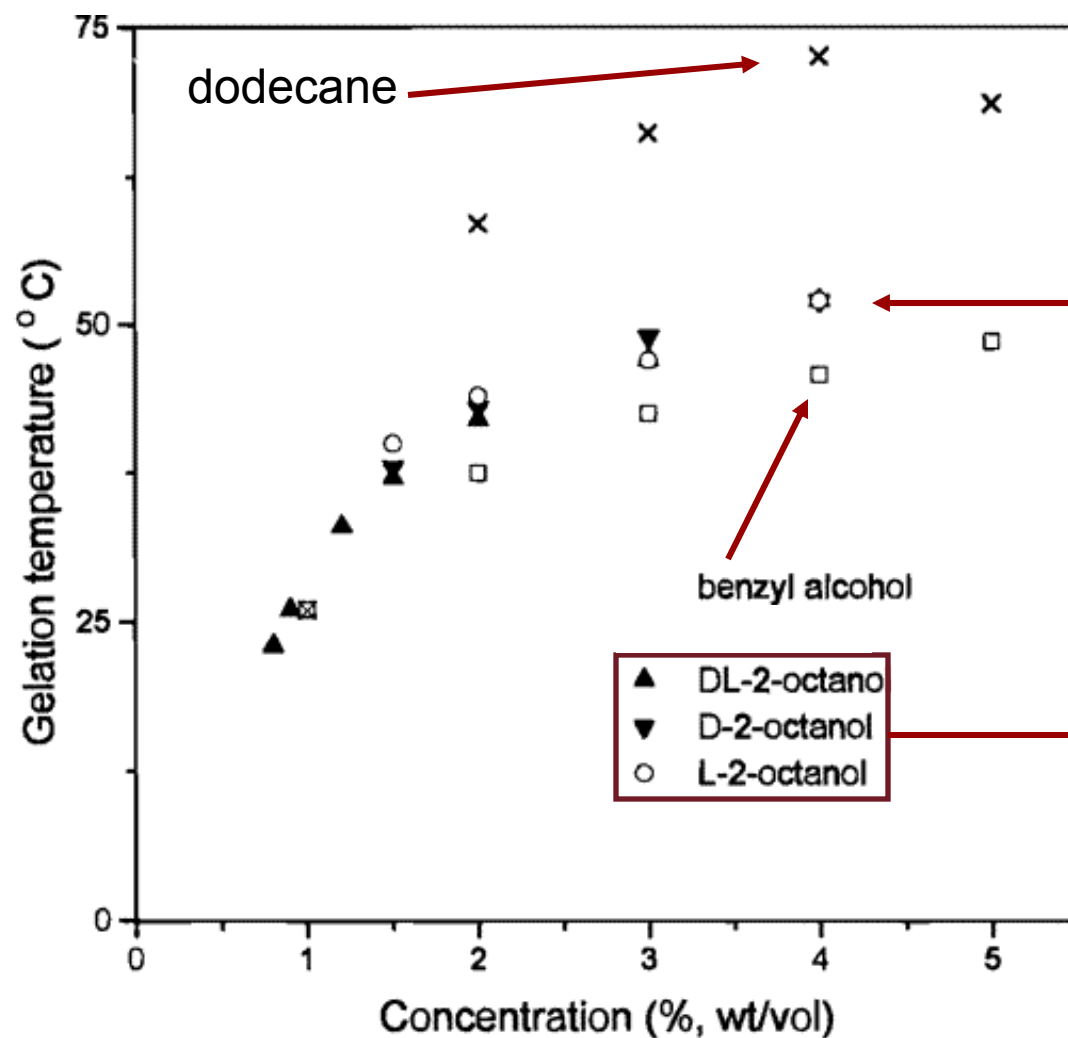


Fig. 5. Conformational representation of the helical reversal in poly(ethyl isocyanate) calculated in (18).

**Green, Peterson, Sato,
Teramoto, Cook, Lifson
Science 1995, 268, 1860.**

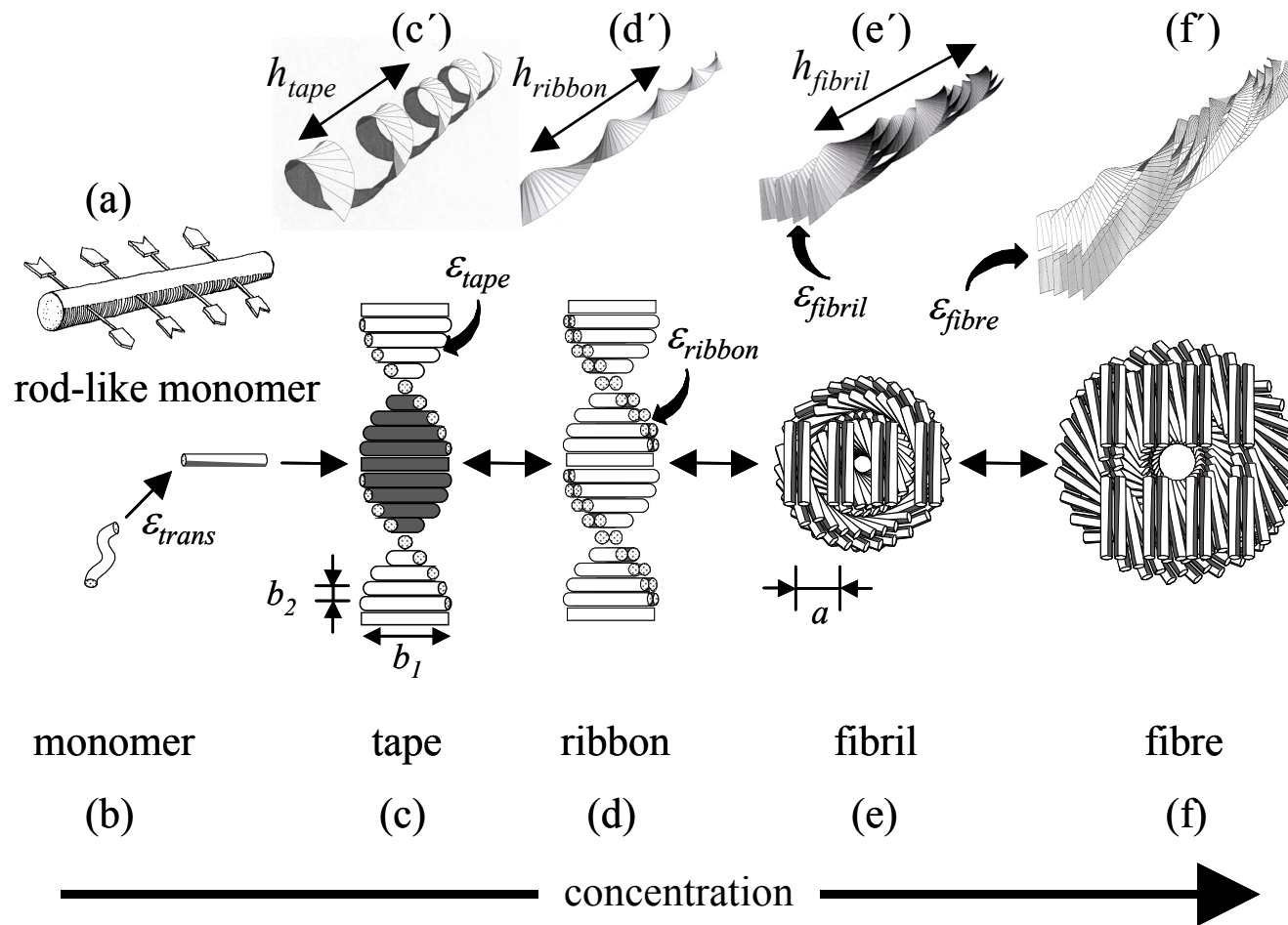
2 wt% CAQB in DL-2-octanol. Nearly identical spectra obtained in D- or L-2-octanol



Mukkamala, Weiss *Langmuir* 1996, 12, 1474

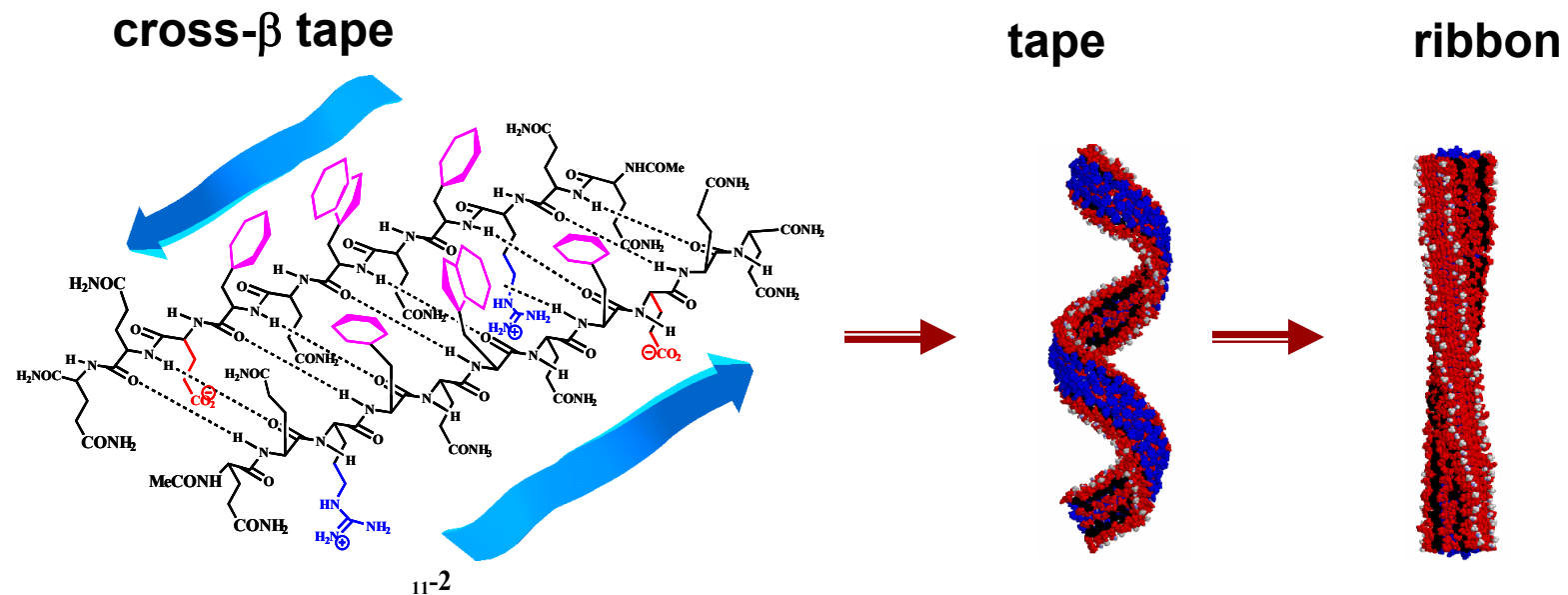
Model of hierarchical self-assembly of chiral rod-like units

For aggregating units with complementary binding sites (such as oligopeptides)



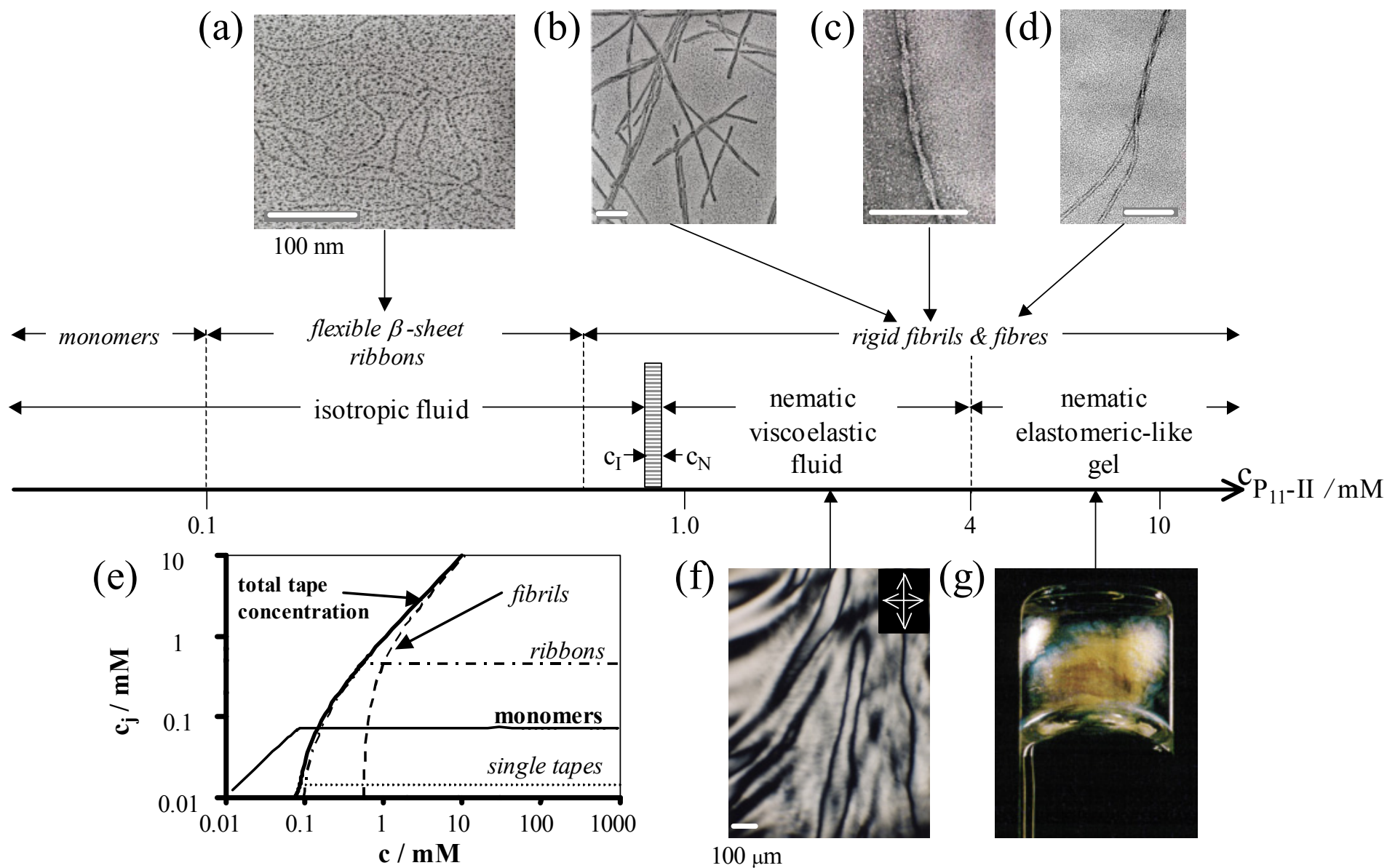
Aggeli et al. *PNAS* 2001, 98, 11857

Molecular dynamics generated P_{11} -II structures at various aggregation stages in water



Aggeli et al. PNAS 2001, 98, 11857

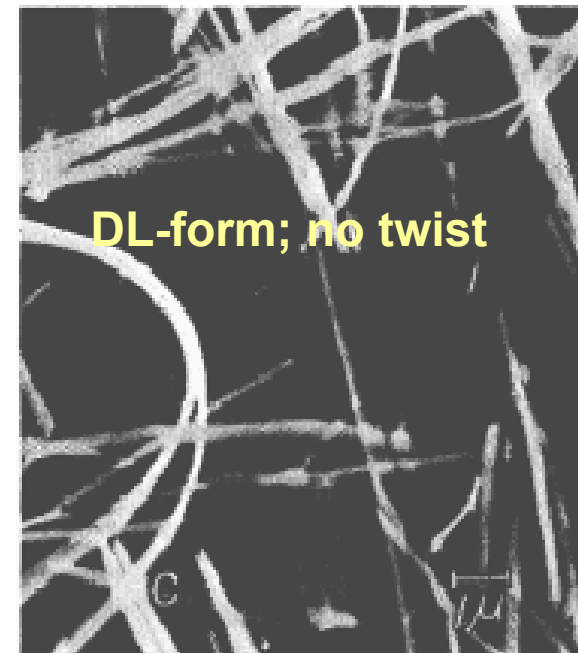
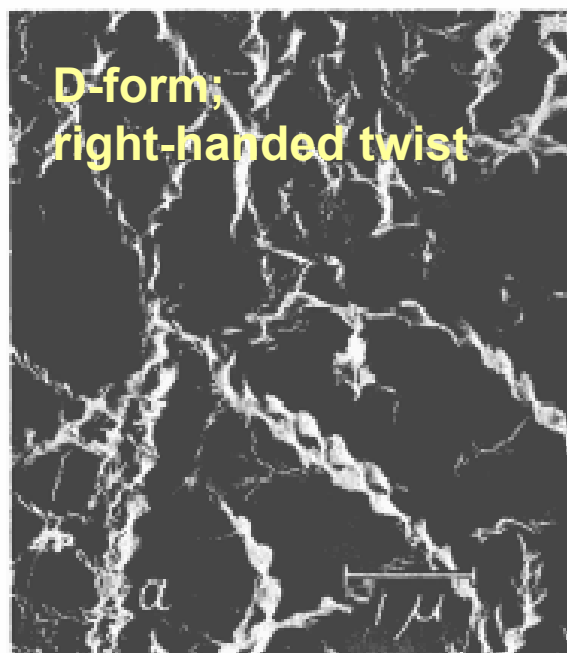
P11-II ($\text{CH}_3\text{CO-Gln-Gln-Arg-Phe-Gln-Trp-Gln-Phe-Glu-Gln-Gln-NH}_2$) in water





12-hydroxystearic acid (HSA) and its salts

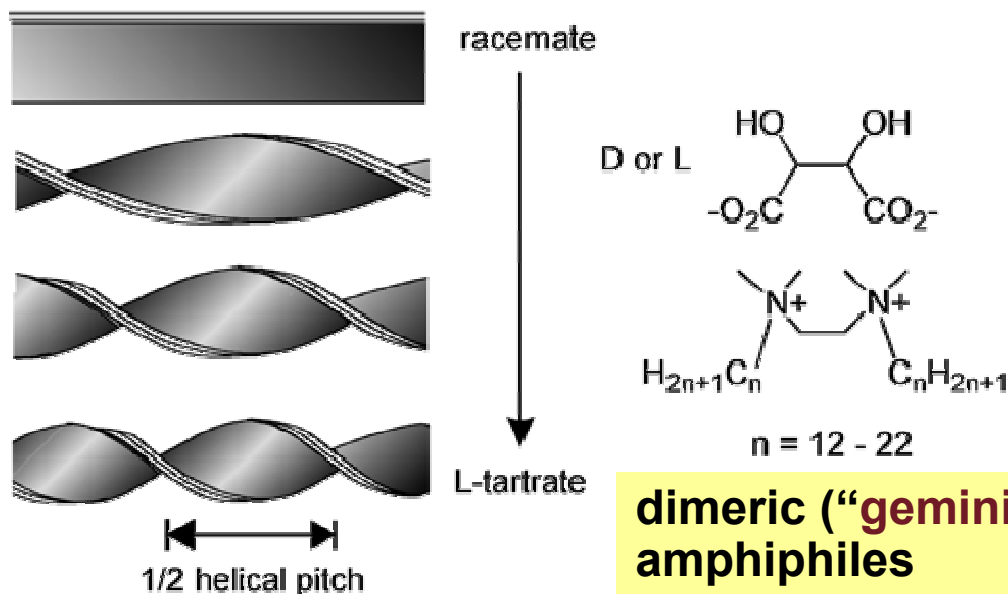
Li⁺ salts prepared from aqueous soaps
(same results with Na, K, Ca, Ba, and Pb soaps)



Tachibana, Kambara *JACS* **1965**, 87, 3015.

Terech, Rodriguez, Barnes, McKenna *Langmuir* 1994, 10, 3406:
No twisted fibers in organic gels with acid!!

Molecular chirality and ribbon twist in 2 component gelator systems in water



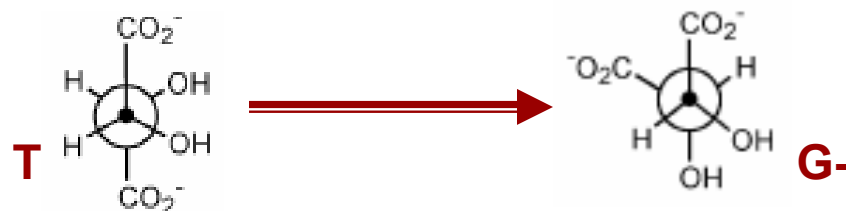
No gel with $n < 13$ or 1 or 3 CH_2 groups between N atoms

dimeric (“gemini”) amphiphiles

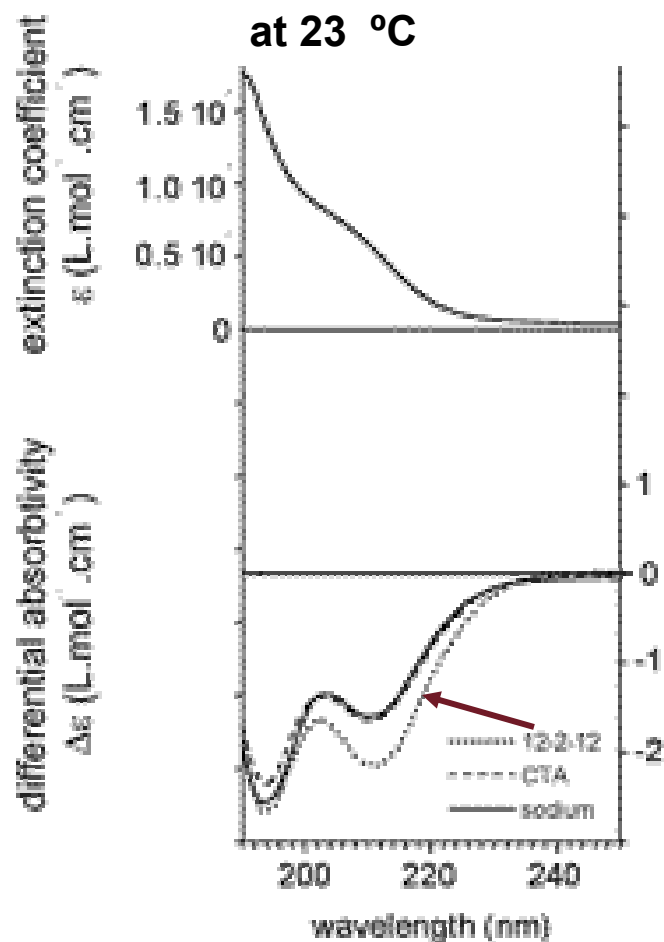
Pitch of ribbons formed in water is tunable by varying the enantiomeric excess of the tartrate.
Helical pitch formed by 16-2-16/L-tartrate = 200 nm.

Berthier, Buffeteau, Leger, Oda, Huc *J. Am. Chem. Soc.* 2002, 124, 13486.

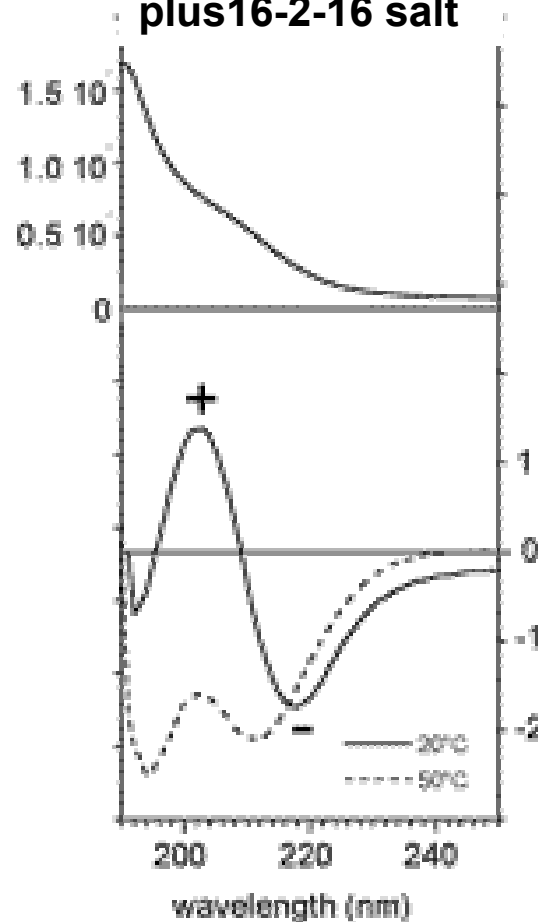
Need a gemini amphiphile that is complementary to chiral tartrate to observe twisted ribbons: switch from T to G- conformations



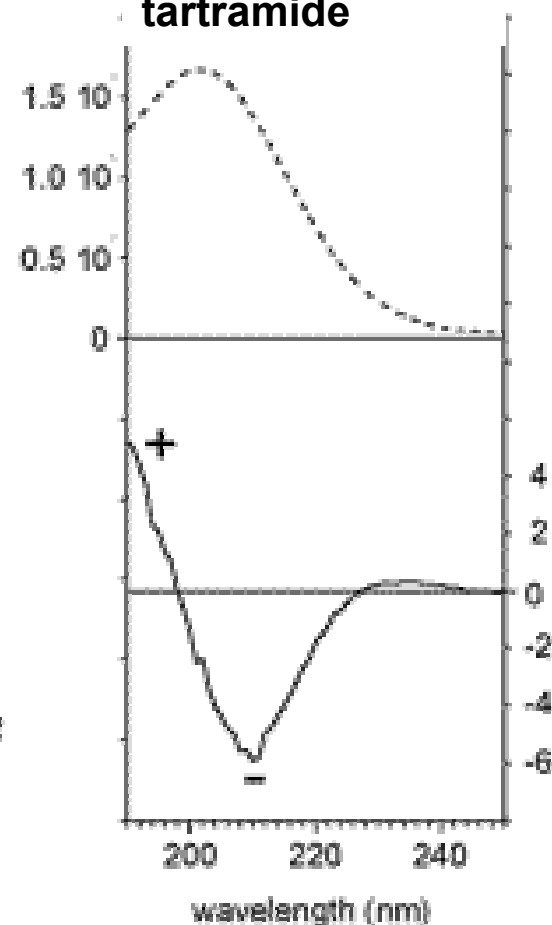
**L-tartrate in water
at 23 °C**



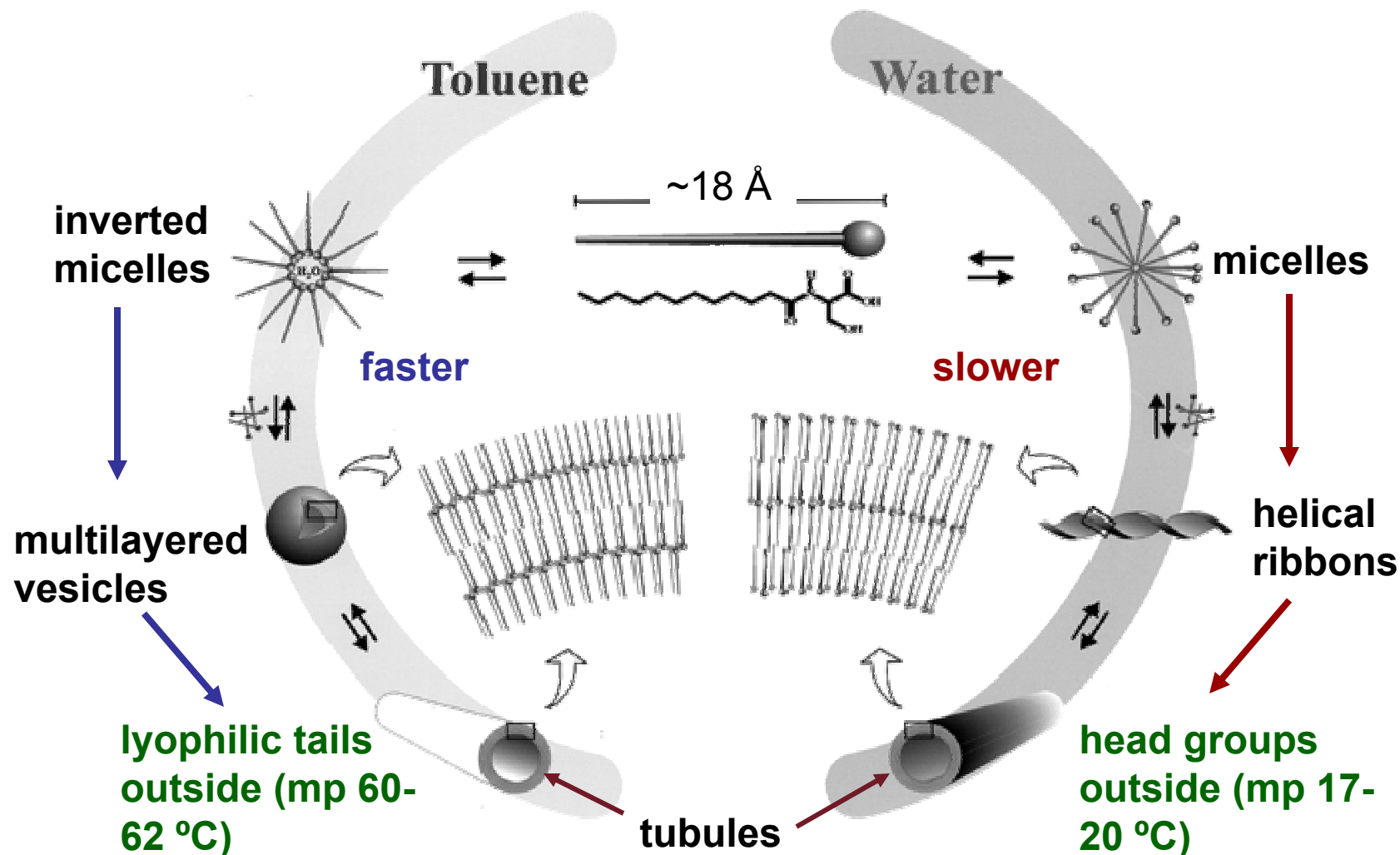
**L-tartrate
plus 16-2-16 salt**



**tetramethyl L-
tartramide**



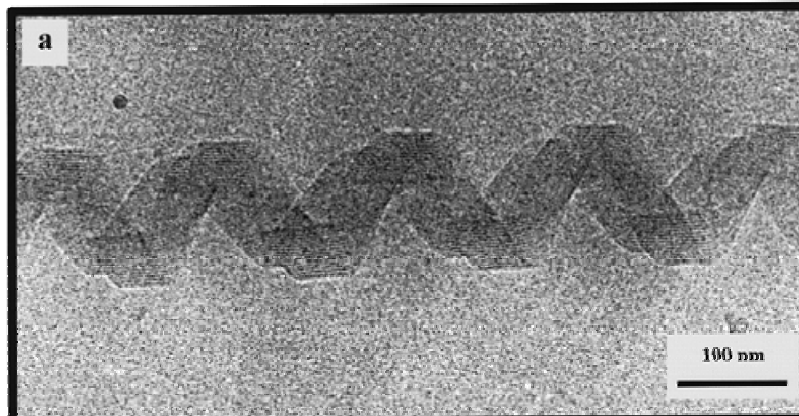
Solvent-dependent aggregation routes to tubules: L-dodecanoylserine



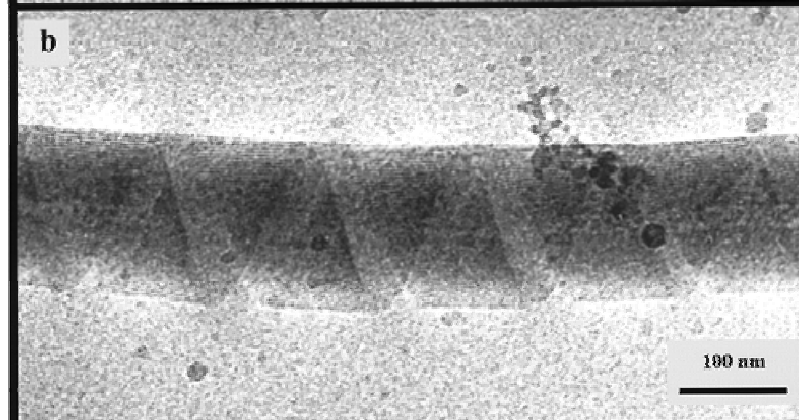
ribbons of racemates not
twisted in water or toluene

Boettcher, Schade, Fuhrhop
Langmuir, 2001, 17, 873.

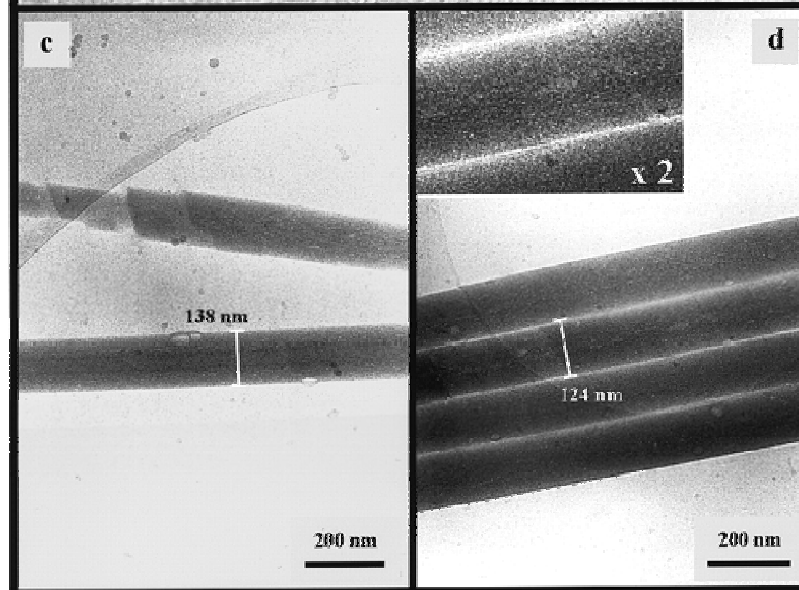
Cryo-TEMs from water (pH 6.4)



multilamellar helical ribbons



intermediate from ribbons to closed tubules

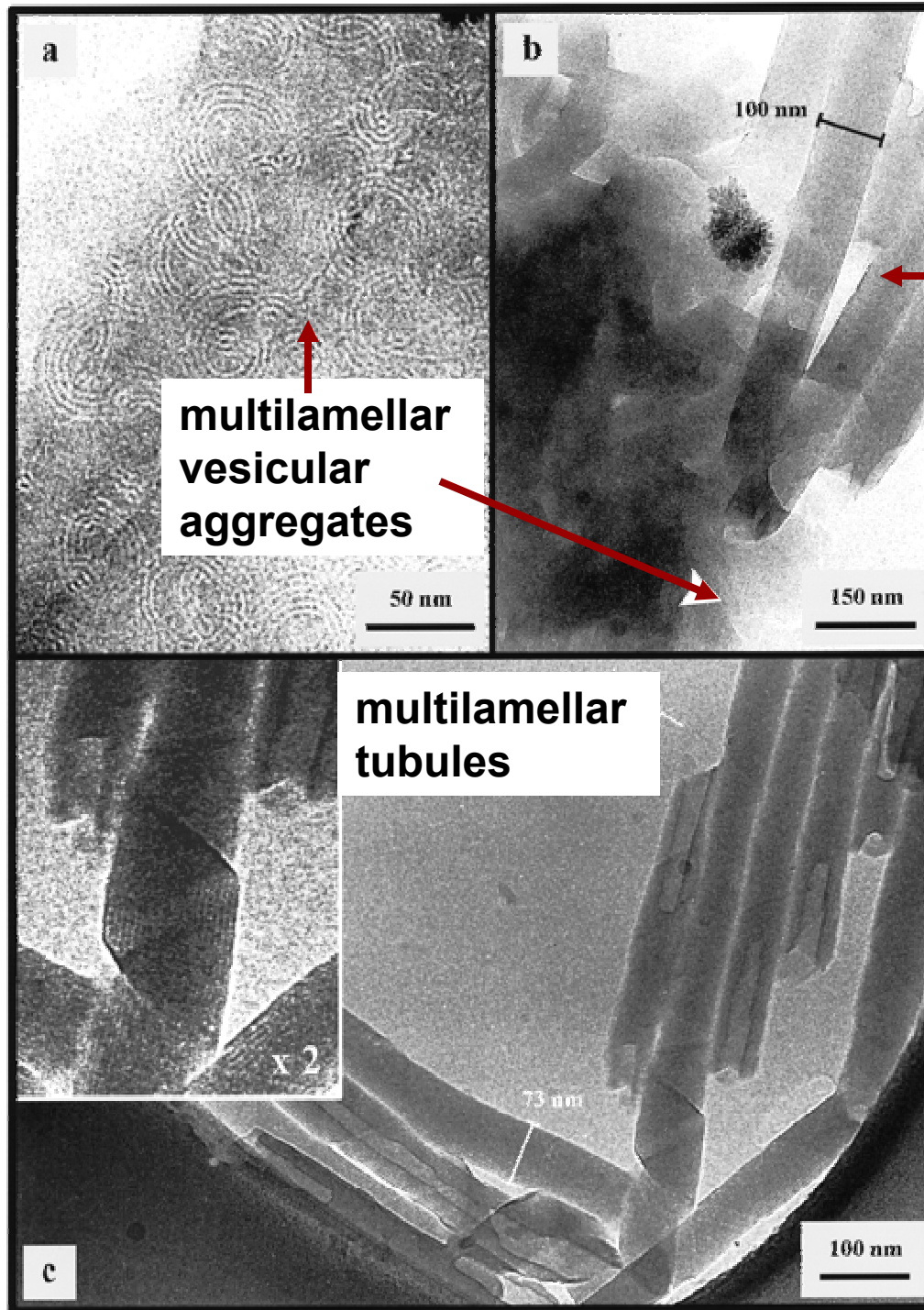


smooth tubular rods (pH 4.9)

tubules stable only at pH 4.9-6.4: where amide and $\text{COO}\cdots\text{HOOC}$ hydrogen bonds occur simultaneously

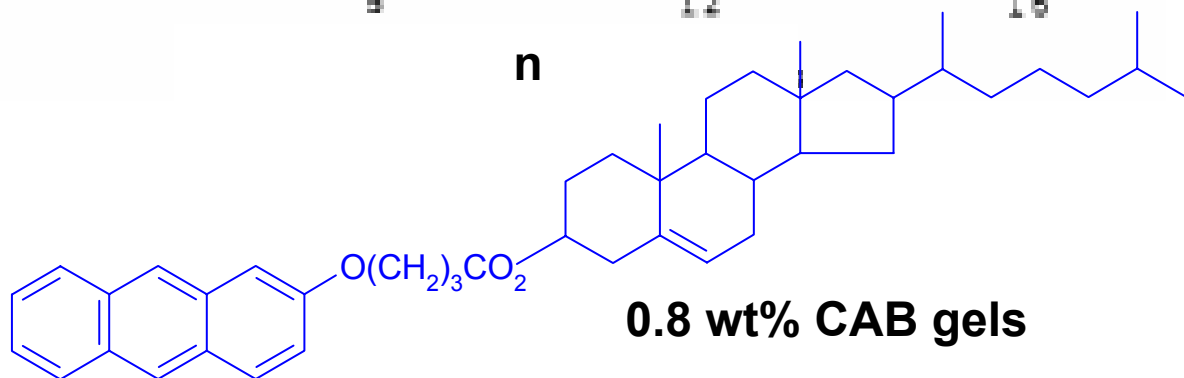
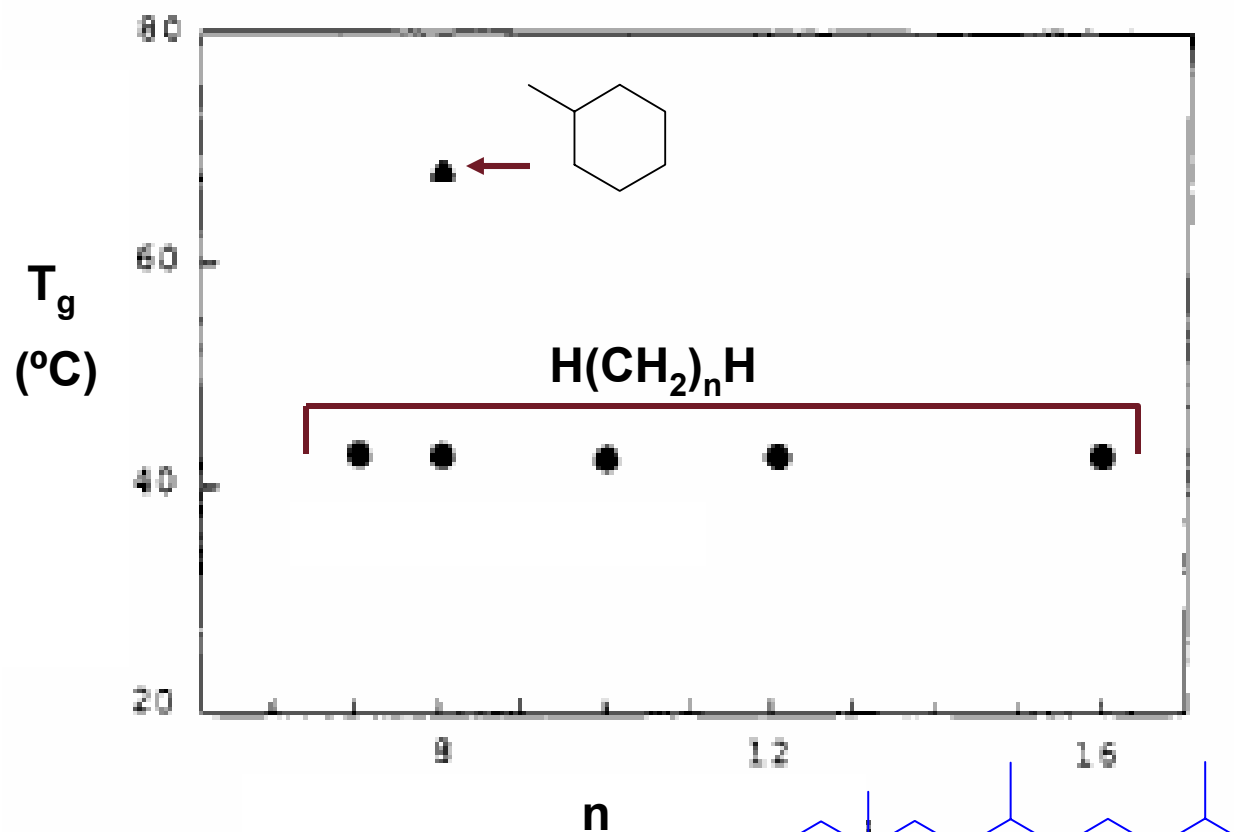
multilamellar tubules

Cryo-TEMs from toluene



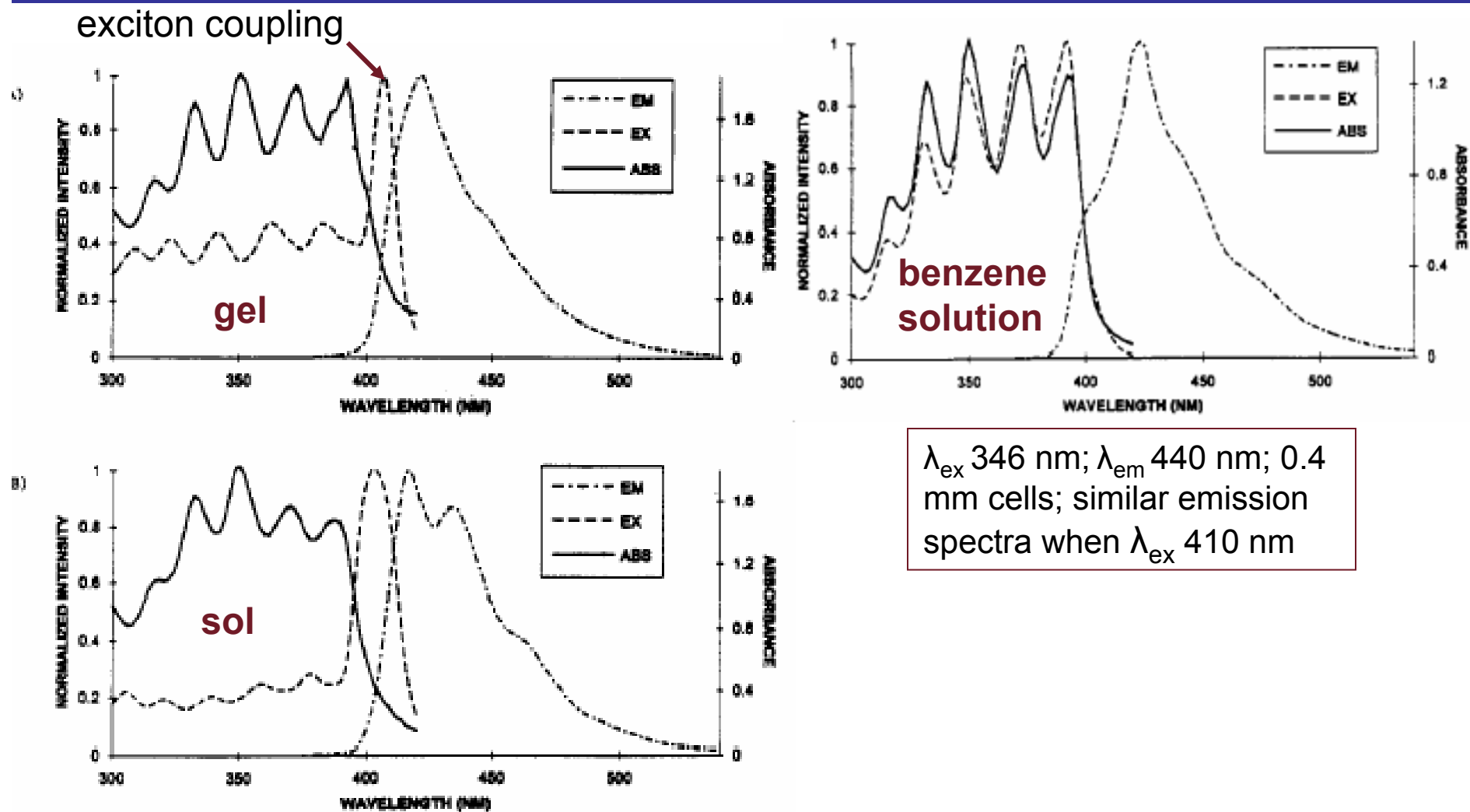
multilamellar tubules

Influence of shape and functionality of non-aqueous media on non-ionic gelator SAFINs



Lin, Kachar,
Weiss, *J. Am.
Chem. Soc.* 1989,
111, 5542.

Normalized absorption (0.7-0.8 wt%), emission, and excitation (1.5 wt%) spectra of CAB



λ_{ex} 346 nm; λ_{em} 440 nm; 0.4 mm cells; similar emission spectra when λ_{ex} 410 nm

hexadecane (*similar spectra in 1-octanol*)

Furman, Weiss *Langmuir* 1993, 9, 2084

Is H-bonding or solvent polarity more important?

Data indicate one form of CAB gel or another formed—no mixtures!!

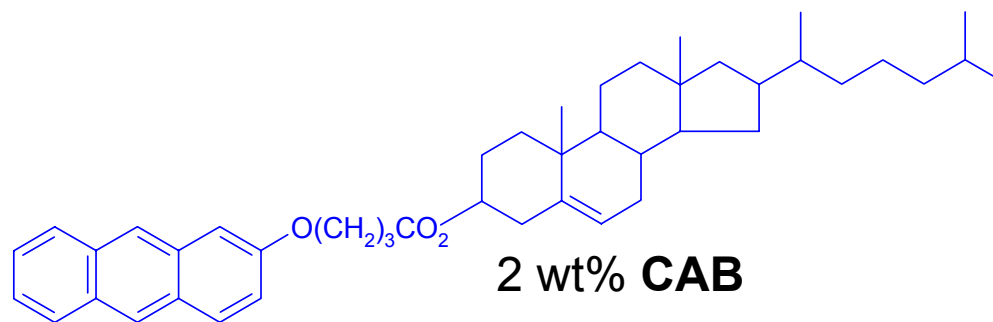
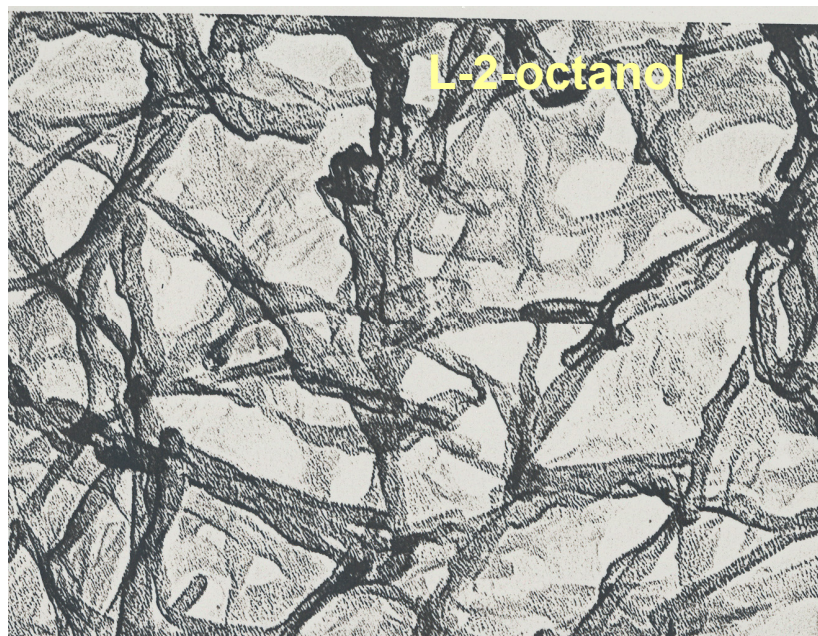
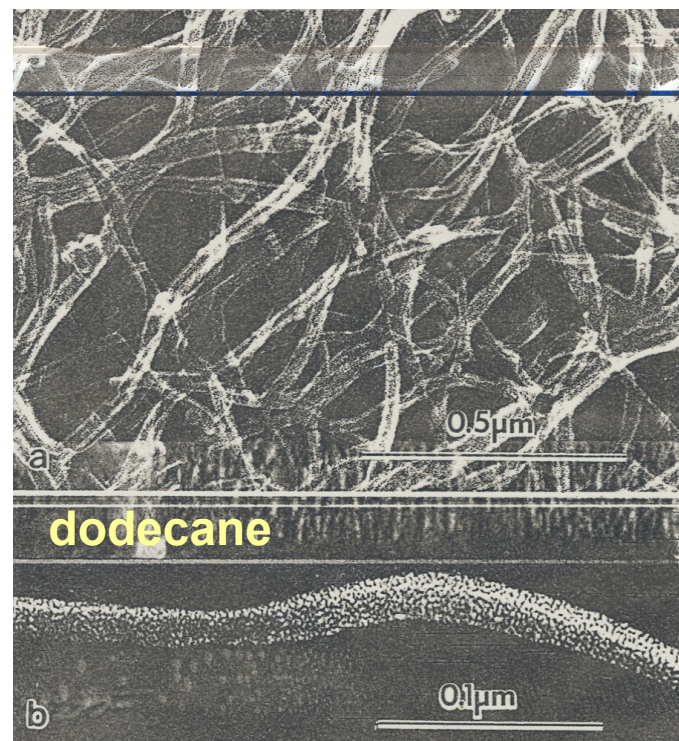
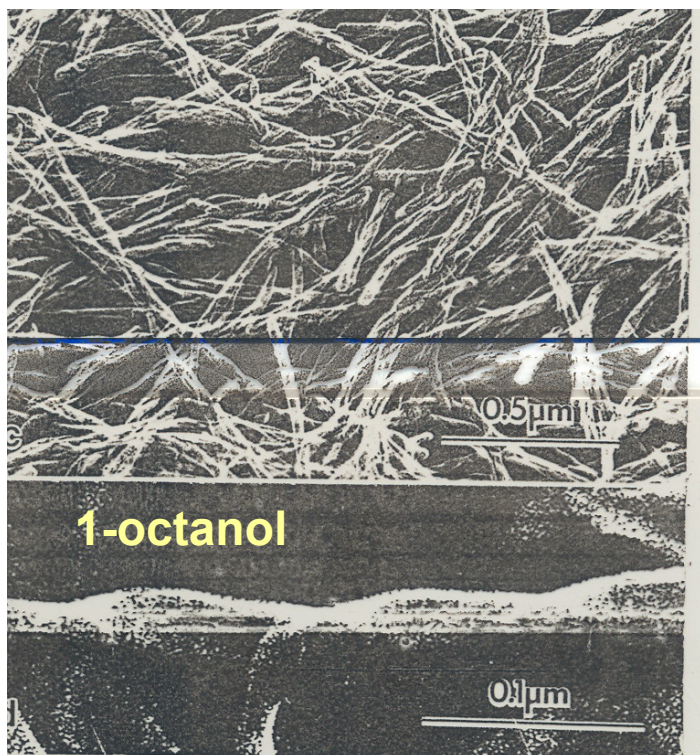
Kinetics and thermodynamics are both important.

wt % CAB	wt % 1-octanol in hexadecane	emission maxima (nm)		T_g (°C) ^b
		gel	isotrop	
1.52	0	421	416	39
1.40	1	421	416	
1.57	3	421	417	
1.46	5	421	416	
1.50	7	421	418	
1.50	10	422	419	
1.44	15	422	417	
1.50	30	422	417	
1.52	50	422	419	
1.50	75	421	420	38
1.56	80	422 ^d	419	42
		427 ^e	419	60
1.38	85	422 ^d	419	42
		427 ^e	419	59
1.60	89	427	421	59
1.50	100	427	421	62
1.51	benzene		422	

independent
of cooling
rate

fast cooled
(~8 °C/min)

slow cooled
(~0.5 °C/min)



Lin, Kachar, Weiss, *J. Am. Chem. Soc.*
1989, 111, 5542.

I get by with a **lot** of help from my friends

Georgetown

Yih-Chyuan Lin

Inna Furman

Ravi Mukkamala

Liangde Lu

Emanuele Ostuni

Emiliano Carretti

David Abdallah

Mathew George

Xiao Huang

Pierre Terech-CEA,
Grenoble

Charlie Glinka-NIST

Vijay John-Tulane

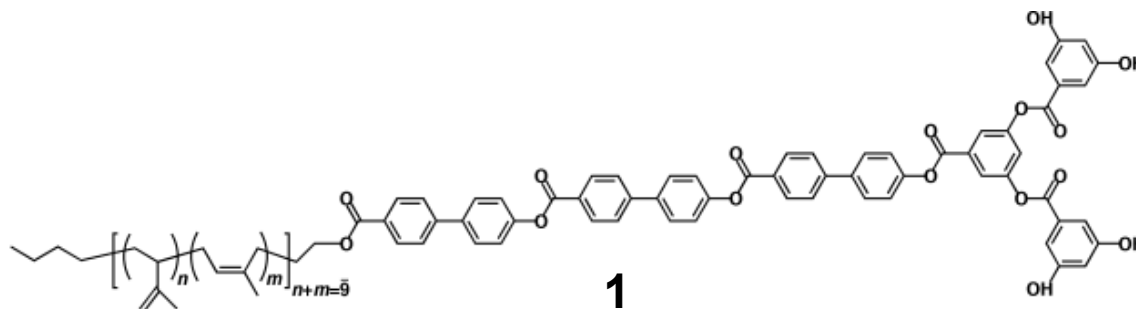
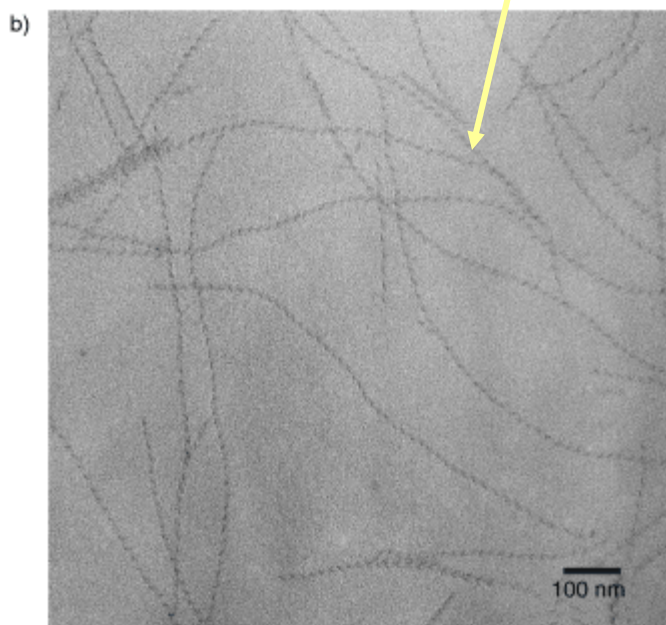
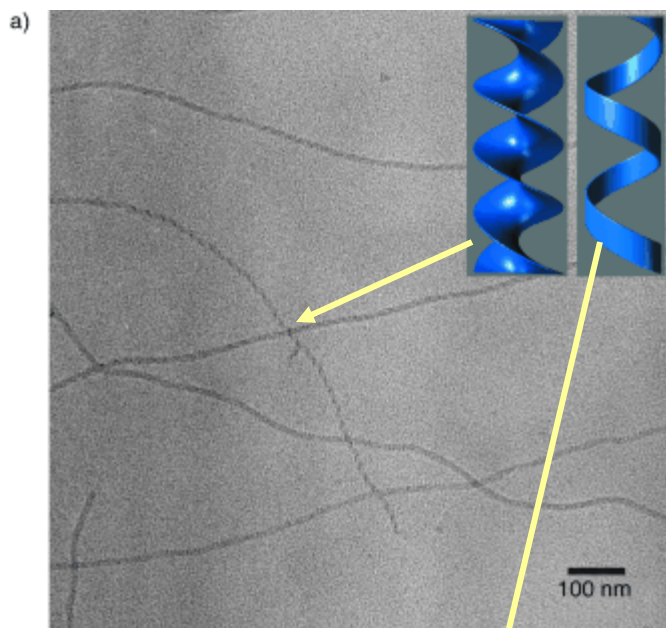
Luigi Dei-Florence

Srini Raghavan-UMd

\$\$ NSF



Twisting depends on surface and edge interaction energies with liquid



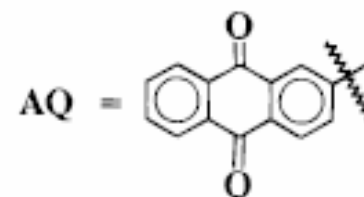
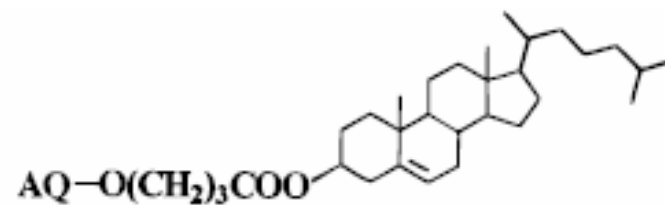
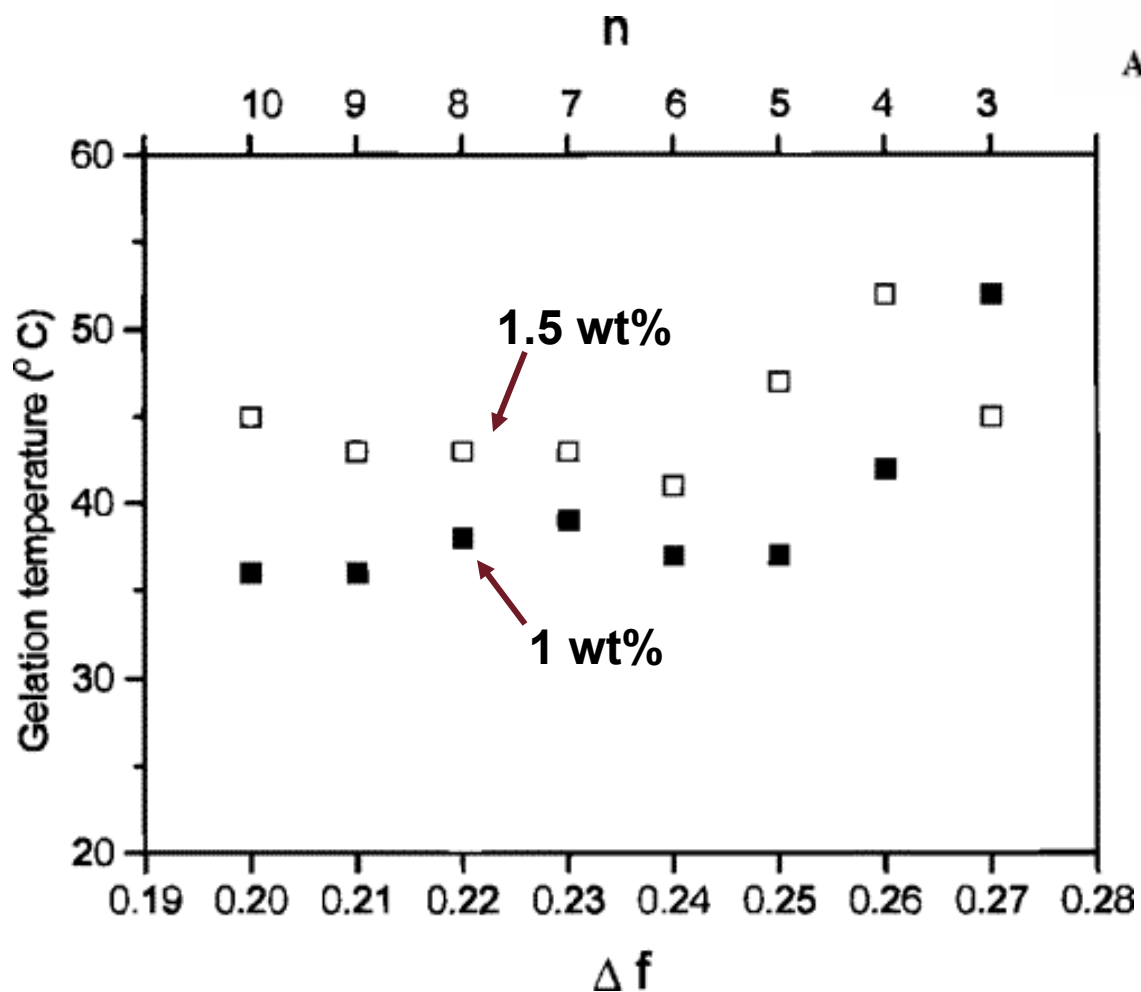
TEM of 5 wt % **1** nanoribbon formed in ethyl methacrylate gel (both left and right hand twists observed); ~3nm cross-sections

Ribbons completely unwound in CH_2Cl_2 !! (2nm X 10nm cross-sections)

TEM after addition of 1.5 wt% of a 0.2 M solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ in THF

Sone, Zubarev, Stupp *Angew. Chem. Intern. Ed.* 2002, 41, 1705.

$H(CH_2)_nOH$ as solvent



Lippert polarity function:

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$$

Mukkamala, Weiss *Langmuir*
1996, 12, 1474