

Healing Gels

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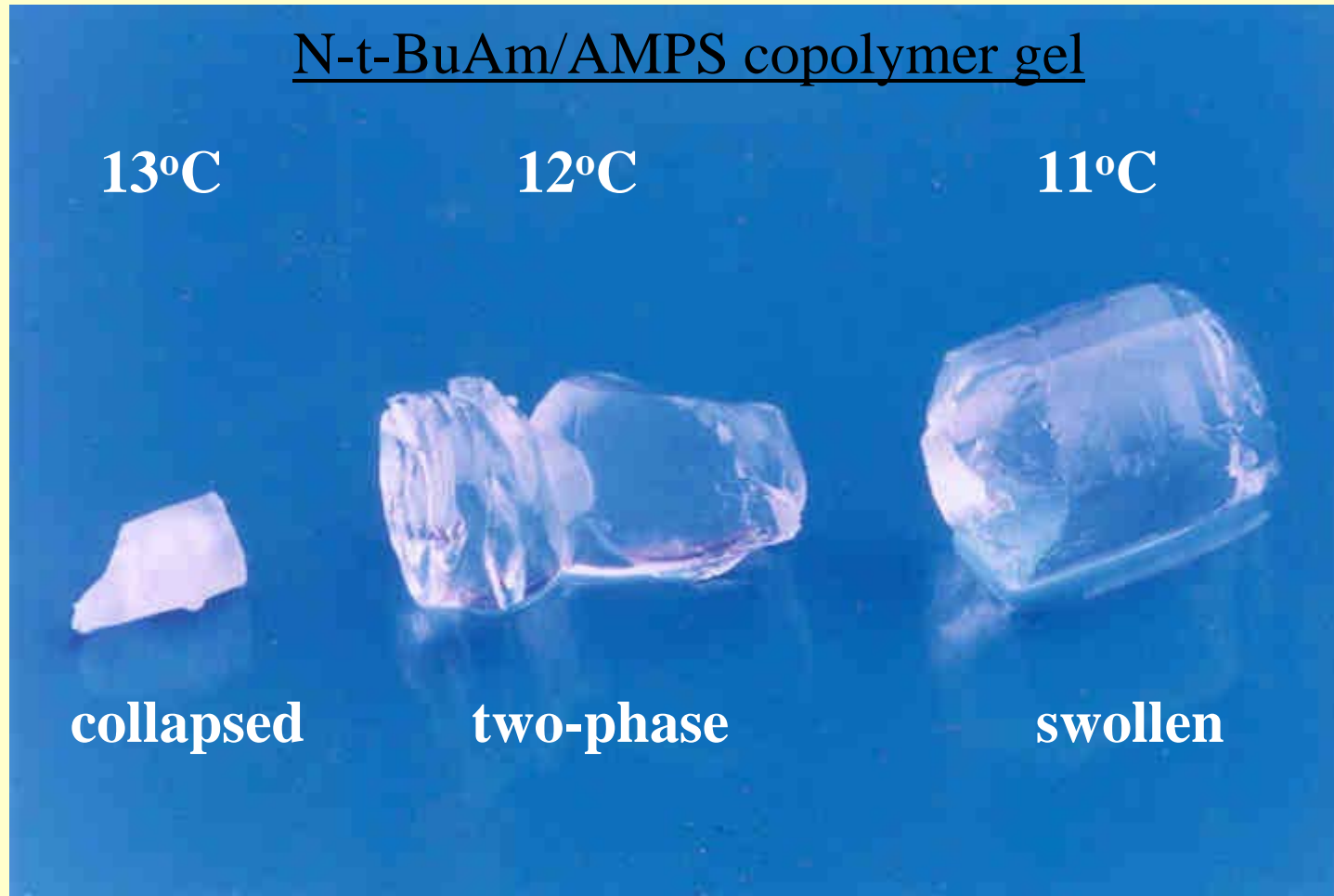
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Acknowledgements: M V Badiger, Vaishali Shinde, Murali Shastry, Darbha Srinivas

This presentation is really about:

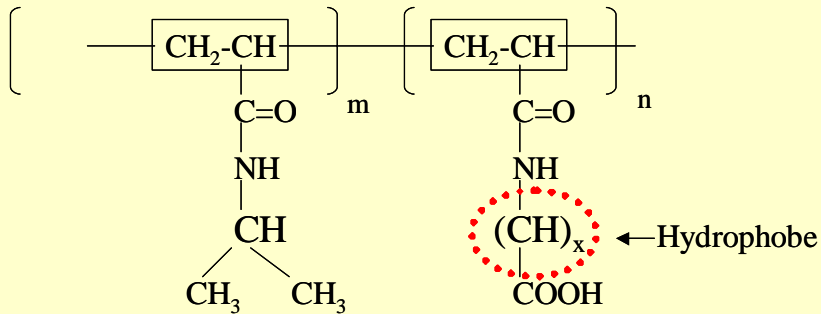
- Lessons learnt from our experiences with “serendipity”
- Watchfulness of the researcher
- Fun doing science

VPT in thermoreversible hydrogels:

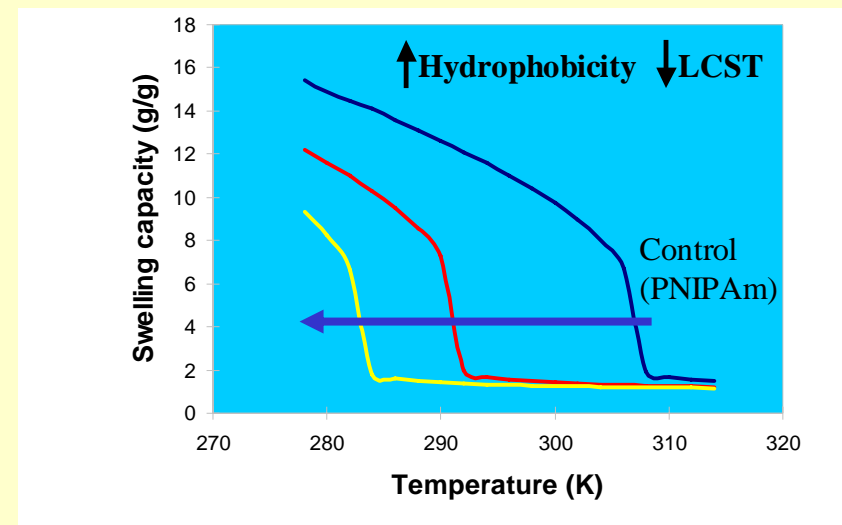
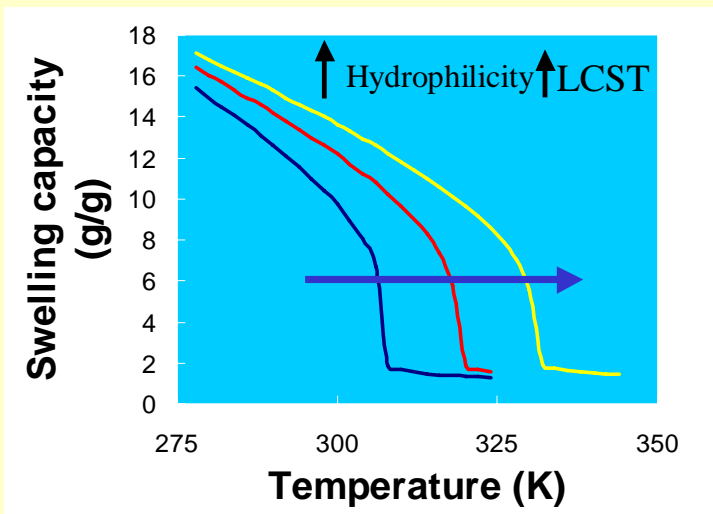
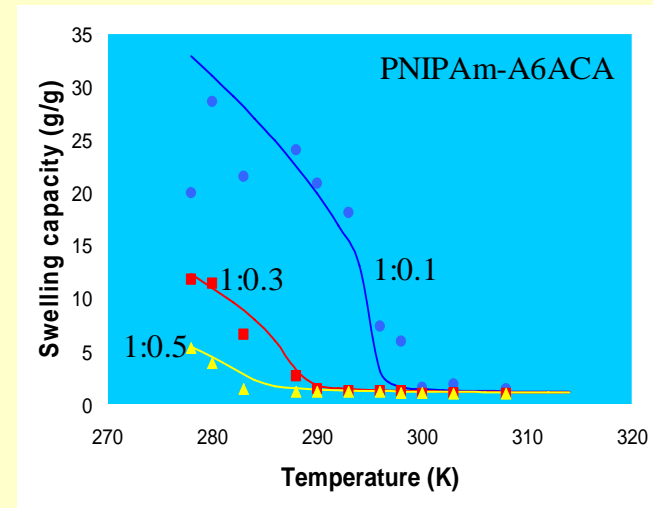


Varghese et al. *J. Chem. Phys.*, 112, 3063 (2000)

The story begins with our interest in:

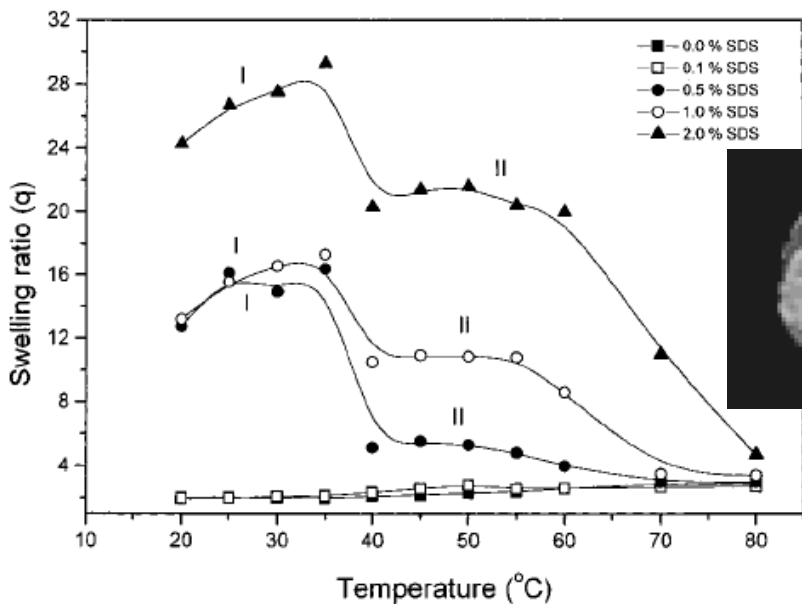
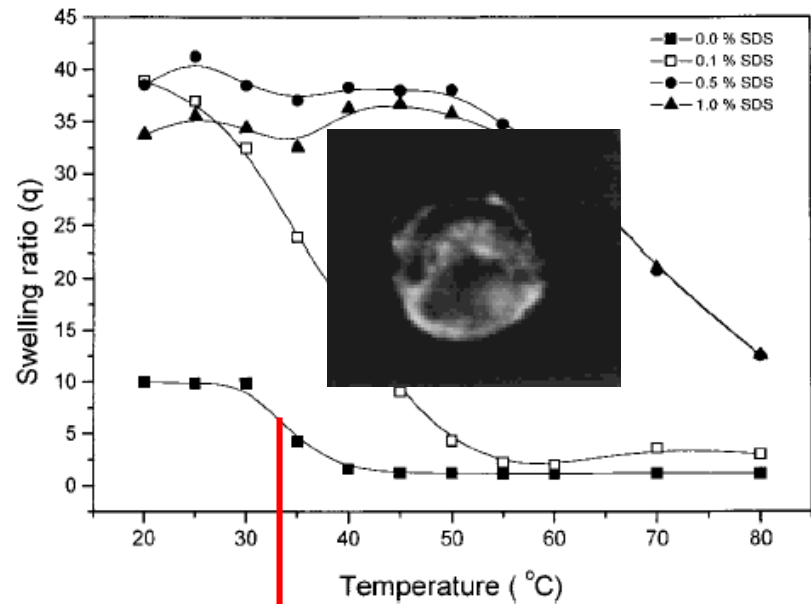
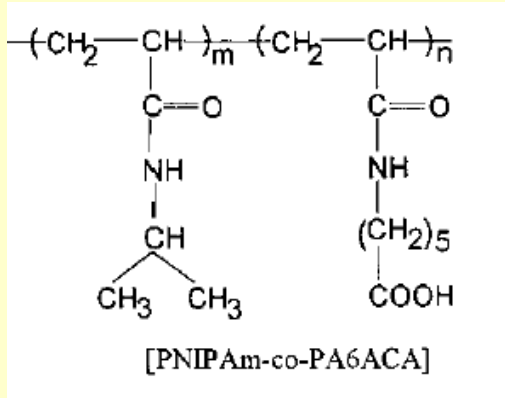


$x=3$: A4ACA
 $x=5$: A6ACA
 $x=10$: A11ACA



Badiger et al. *J. Chem. Phys.*, **109**, 1175 (1998)

More with these gels



→ VPT in PNIPAm gel

Skin-core morphology & Double VPT's induced by surfactants

Bhalerao et al. *Langmuir*, 17, 2585 (2001)

The accident.....



Gel dried in a “new”
oven



Gel dried in an “old”
oven

Pursuing the why & how?

Metal complexation: A new stimuli for VPT

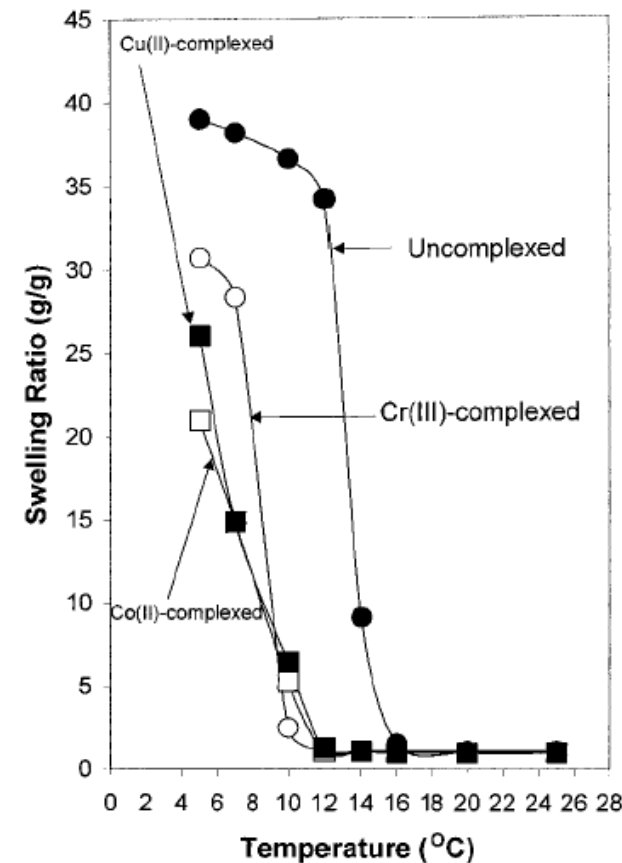
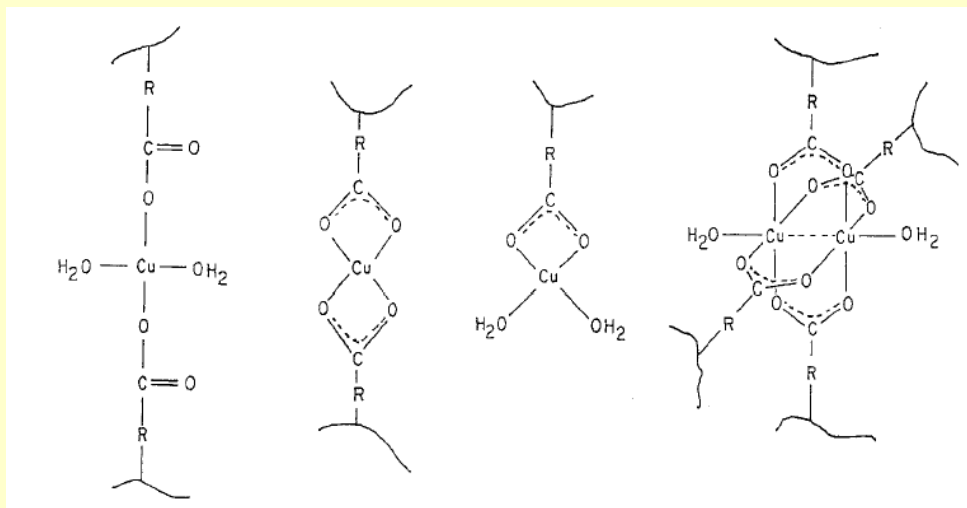


TABLE 1: Swelling Behavior of Polyacid Gels in Water and CuCl_2 Solutions

gel	swelling ratio in water ^a (g/g)	swelling ratio in CuCl_2^a (g/g)	amt of Cu(II) complexed (g mol/g)	% COOH groups complexed ^b	monomeric species ^c	dimeric species ^c
A4Ac(H)	4.4	2.3	1.2×10^{-4}	1.6	<i>d</i>	<i>d</i>
A4Ac(Na/H)	16.3	4.9	1.7×10^{-3}	24	<i>d</i>	<i>d</i>
A4Ac(Na)	24.8	4.8	1.3×10^{-2}	26	<i>d</i>	<i>d</i>
A4ABA(H)	1.1	1.0	5.0×10^{-5}	1.6	<i>d</i>	<i>d</i>
A4ABA(Na/H)	24.9	1.1	9.3×10^{-4}	28	<i>d</i>	<i>d</i>
A4ABA(Na)	98.8	1.0	9.9×10^{-4}	30	<i>d</i>	<i>d</i>
A6ACA(H)	1.0	1.0	5.4×10^{-5}	1.8	<i>d</i>	<i>d</i>
A6ACA(Na/H)	147.0	1.9	2.4×10^{-4}	32	<i>d</i>	<i>d</i>
A6ACA(Na)	230.0	1.0	9.8×10^{-4}	36	<i>d</i>	<i>d</i>
A8ACA(Na)		1.0	9.8×10^{-4}	40	<i>d</i>	<i>d</i>

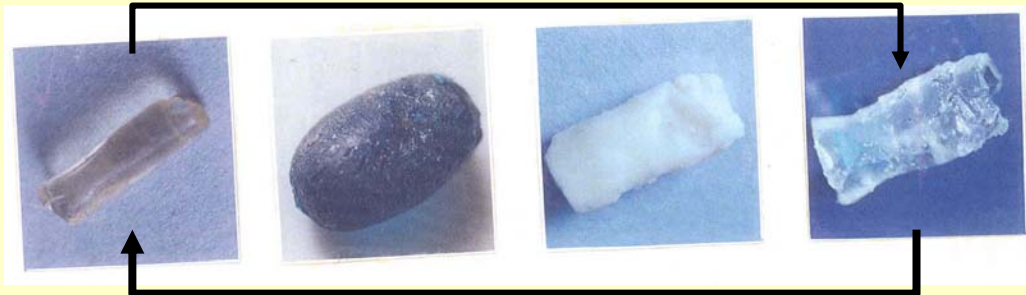
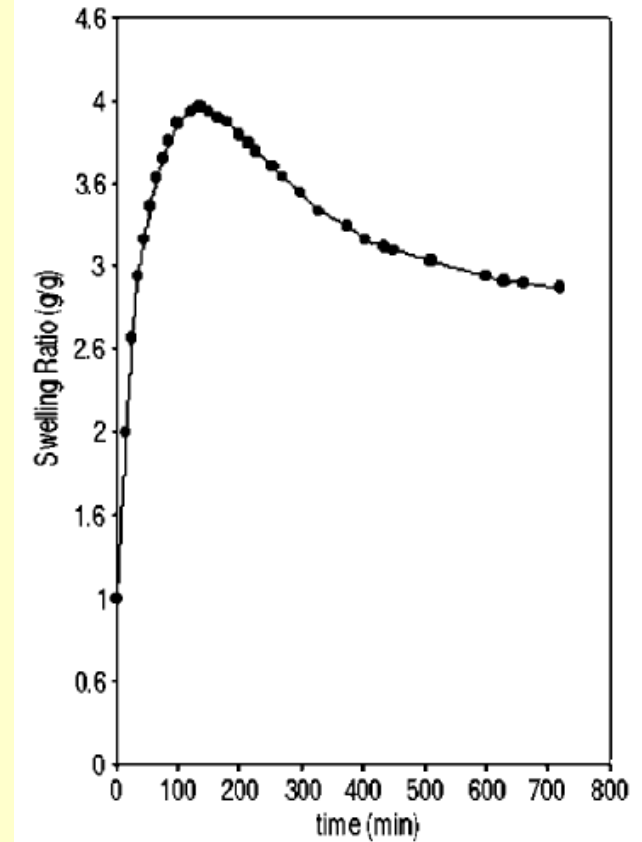
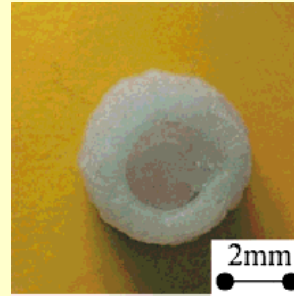
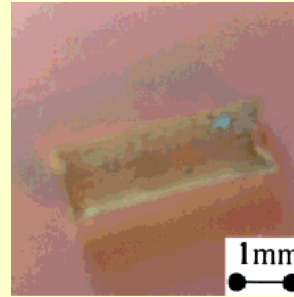
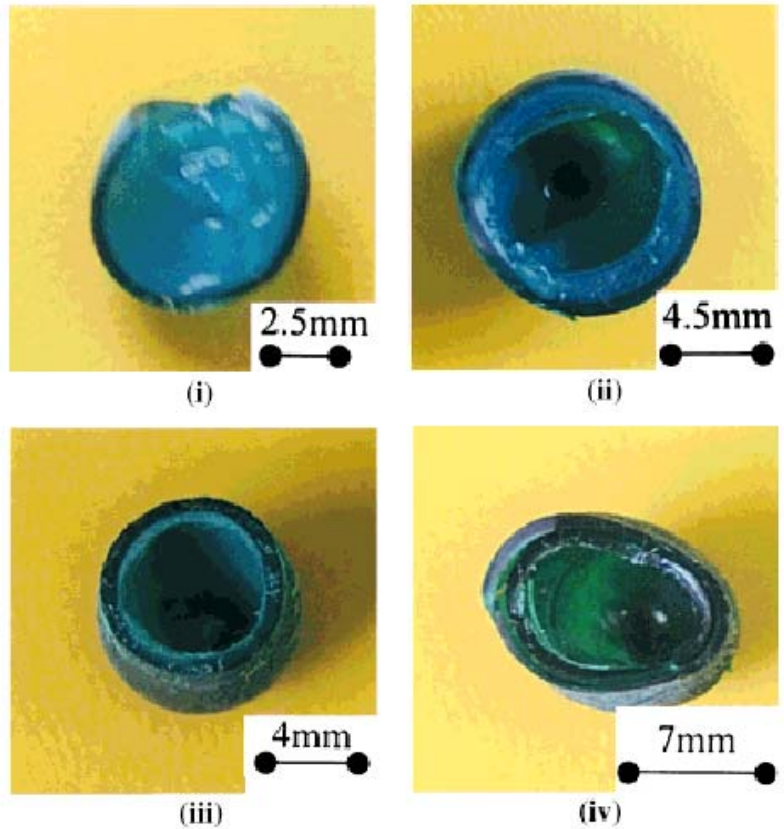
^a Swelling measurements made 4 h after immersion in salt solution. ^b % complexation = $100(\text{gram moles of metal ion complexed})/\text{gram moles of COO}^-$ on dry gel. ^c EPR studies. ^d Present.

Varghese et al.
J. Phys. Chem B, 105, 5368
(2001)

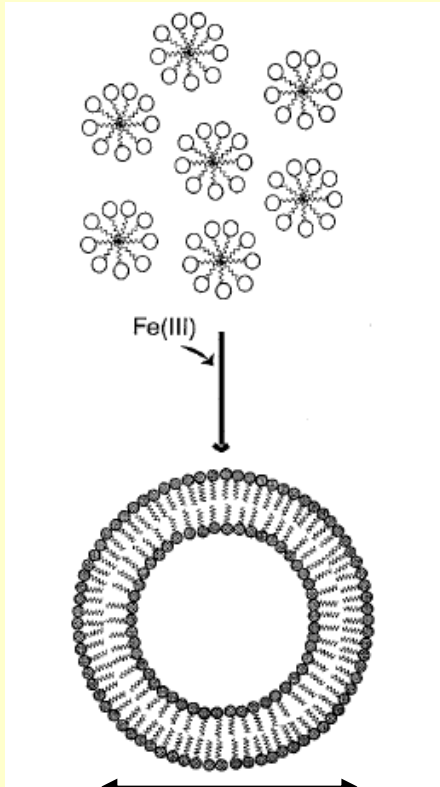
Varghese et al.,
J Phys. Chem, 112, 3063
(2000)

Importance of keeping eyes open!

Varghese et al., *Adv. Matl.*, 13, 1544 (2001)



Self organized hollow objects:



Sidophores



A6ACA gel



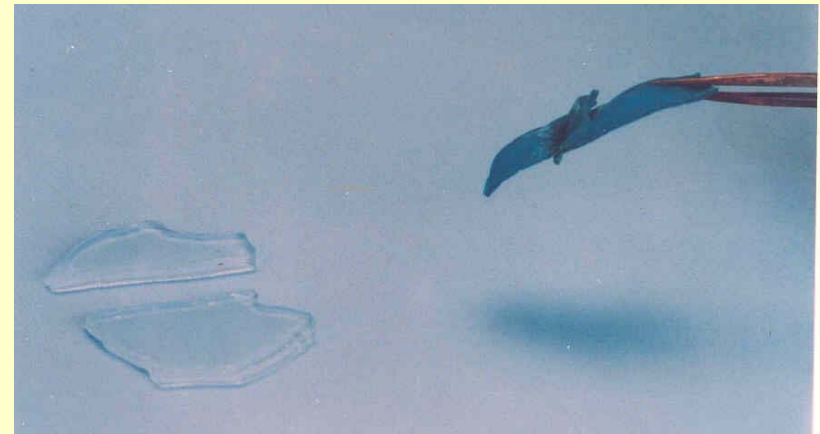
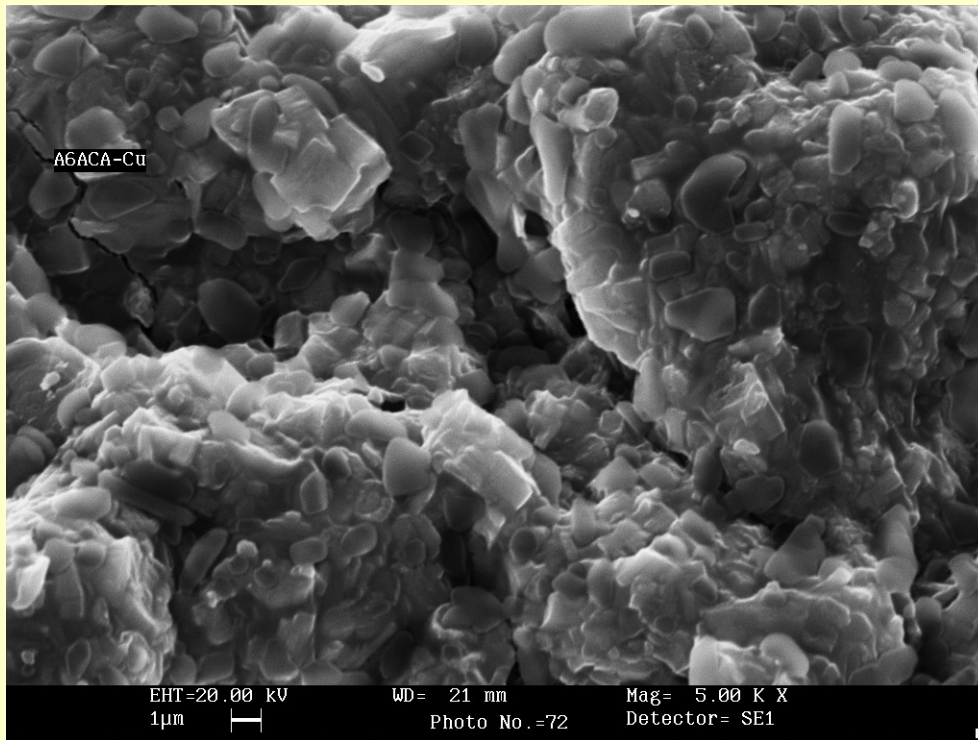
~ 10 cm

Coconut

Accident No. 2:

$t \sim L^2 / D \Rightarrow$ A 0.5mm dia gel should require $\sim 1/100$ of the time required for a 5mm gel to transform into a hollow spherical object

Dry gel \rightarrow grind to fine powder \rightarrow swell in CuCl_2 soln \rightarrow lump (?) \rightarrow sonicate \rightarrow SEM



Progressive healing:



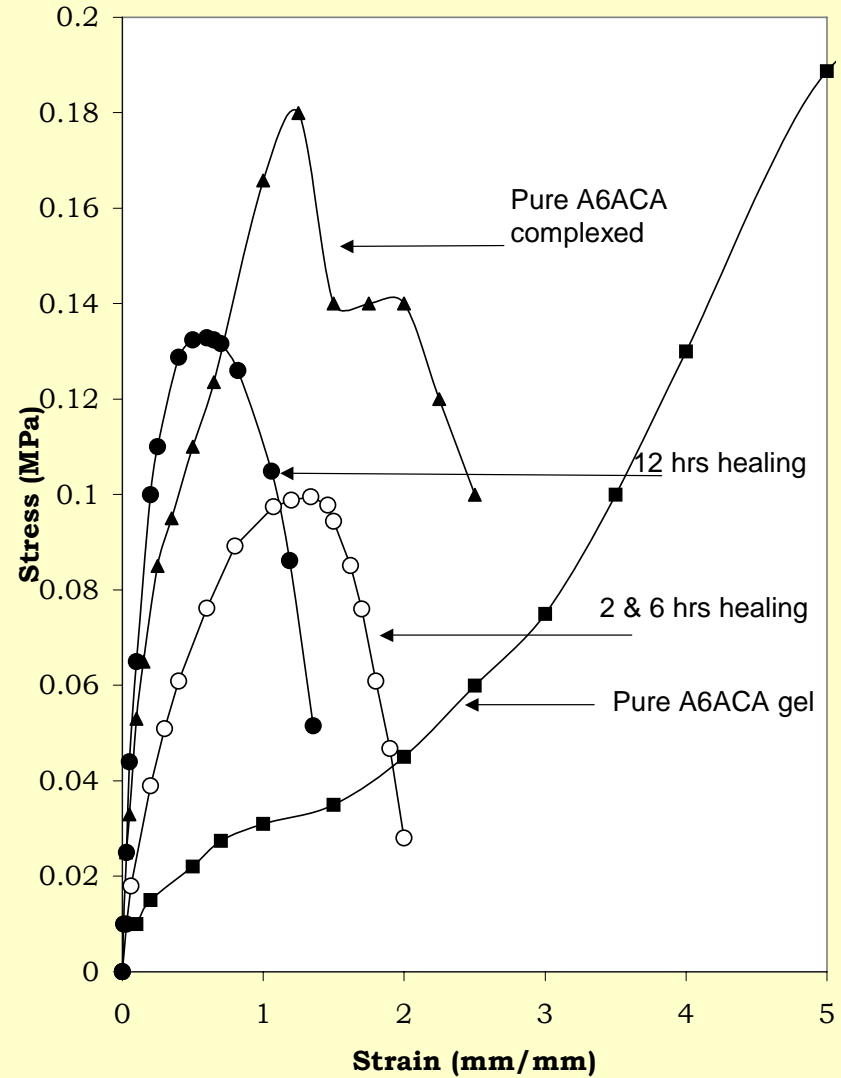
Initial healing



Hydrophobicity-driven reshaping
Deformation-driven healing?



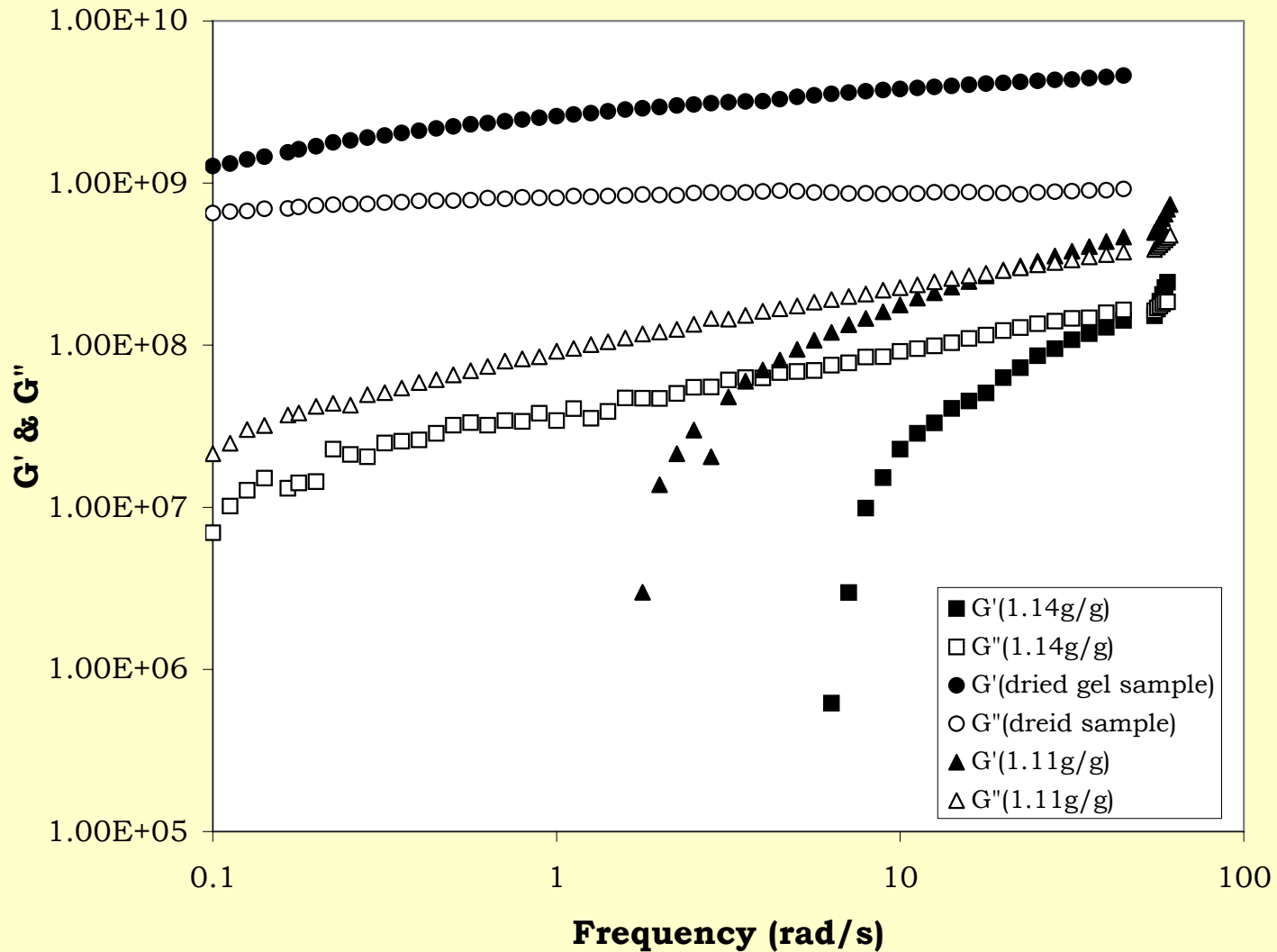
Hollow interior pervades through the weld line



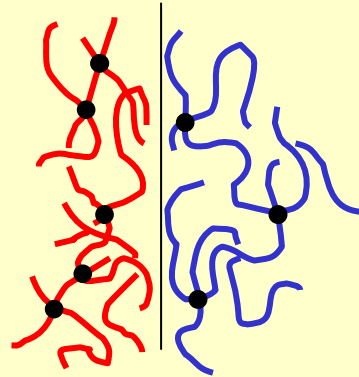
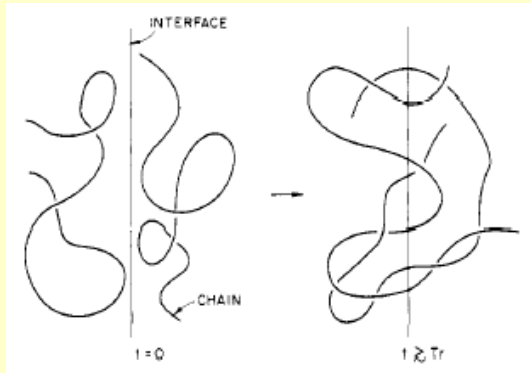
Various scenarios for why gels might progressively heal:

- Initial “molecular” weld line formed via complexation with Cu^{++} across the interface (role of flexible side chains: A6ACA heals better than A4ABA, while AAc does not heal at all)
- Complexation progresses from ‘monomeric’ species to “dimeric” species causing increase in cross-linking degree, thereby increasing weldline strength
- The enthalpic benefit of complexation overrides the entropic costs of deformation causing the gels to deform and heal increasingly larger surface areas thereby increasing weldline strength

Can gels deform easily?



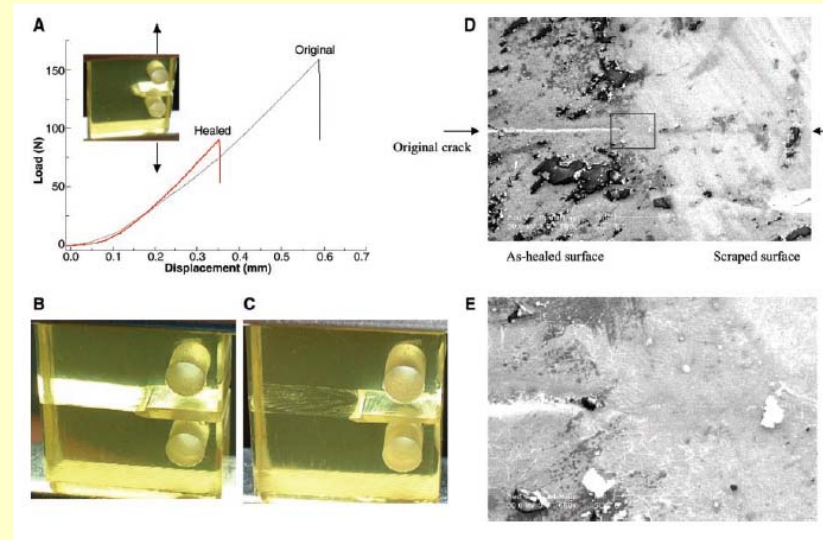
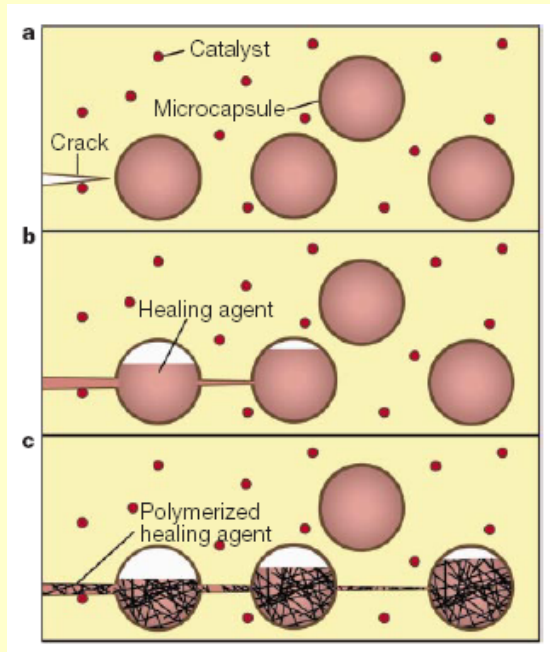
Healing strategies in composites:



Linear polymers weld by reptating across the interface.

Can crosslinked polymers weld?

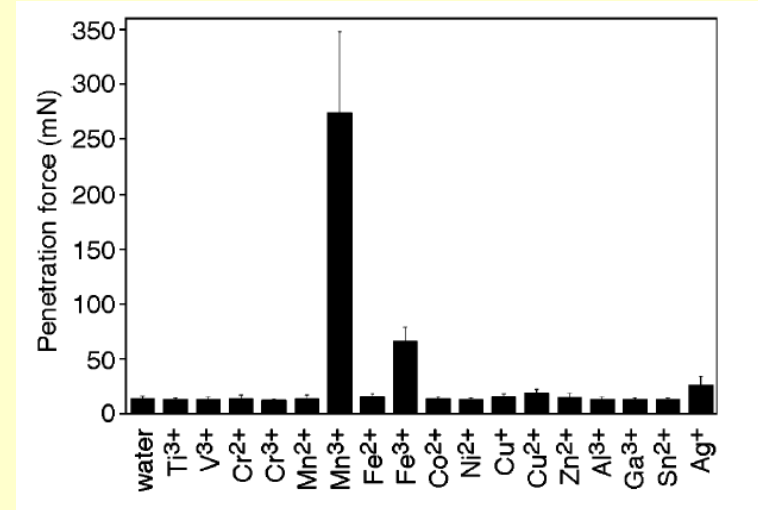
S. R. White et al., Nature 2001, 409, 795



Reversible Diels Alder reaction between multifuran & multi-maleimide functional groups on polymers

X. Chen et al., Science 2002, 295, 1698

Adhesion in marine mussels (gels):



<http://www.delftoutlook.tudelft.nl/info/index.cfm?hoofdstuk=Article&ArtID=3992>
Monahan & Wilker, Langmuir, web release March 19, 2004

Some concluding thoughts:

- Can we design robots with “gel arms” that can “glue” to surfaces and lift them ?
- Can we design paints/coatings that can heal?
- What is the role of the flexible side chains in healing?
- What controls the kinetics of healing?