

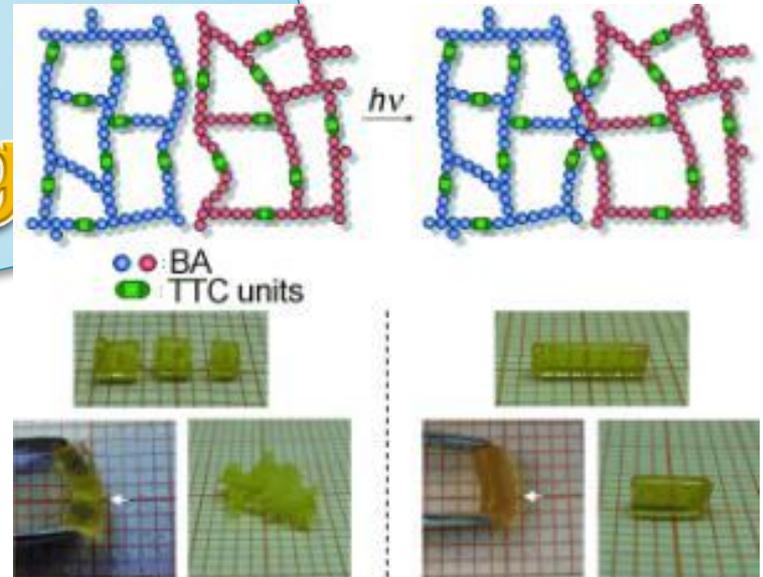
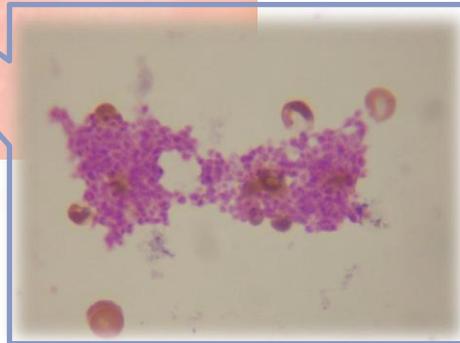


Self-Healing Polymers and Composites

Yufei Wang
Sept. 10th. 2012

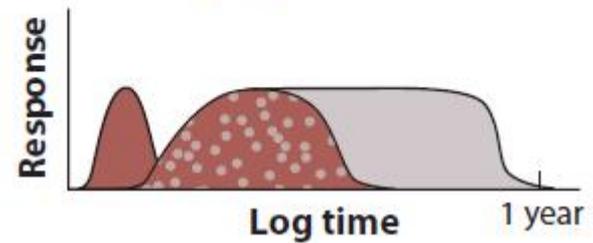
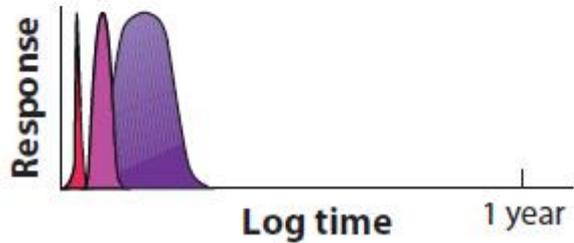
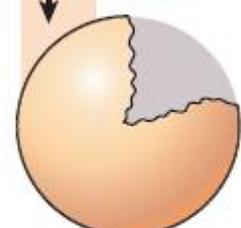
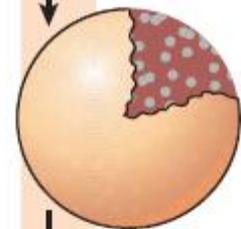
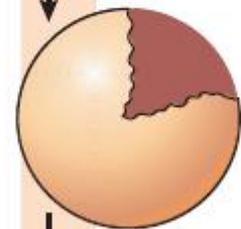
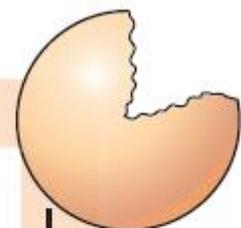
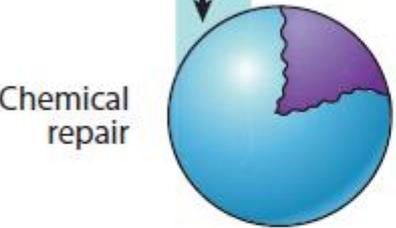
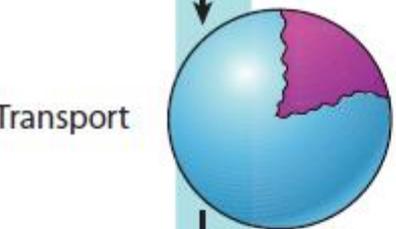
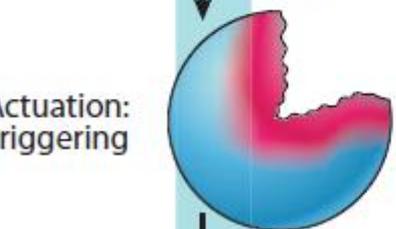
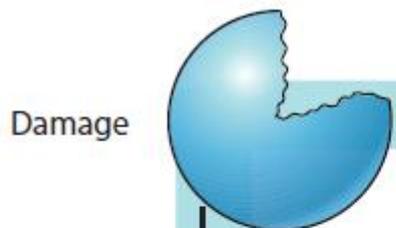
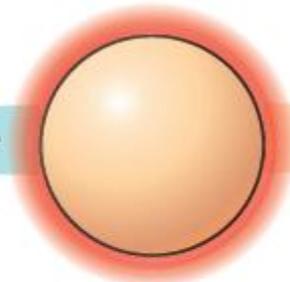


Amazing Self-healing



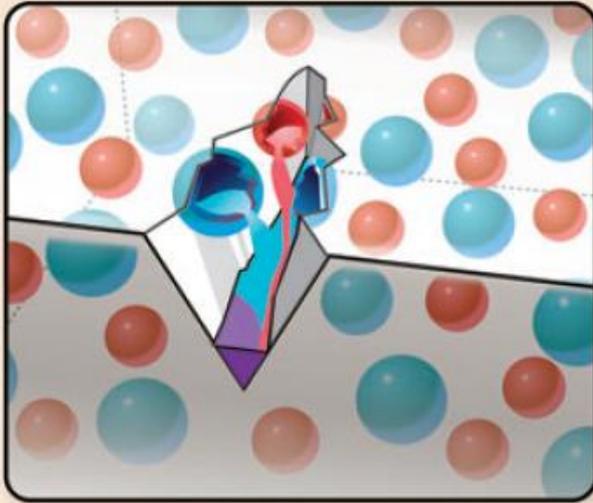
Synthetic route

Biological route

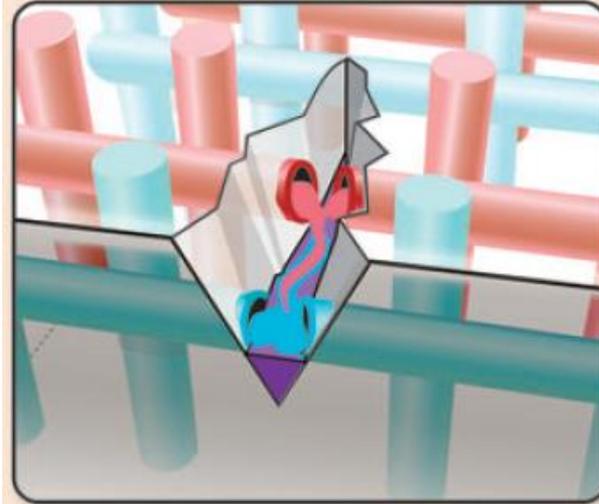


Approaches to Self-Healing

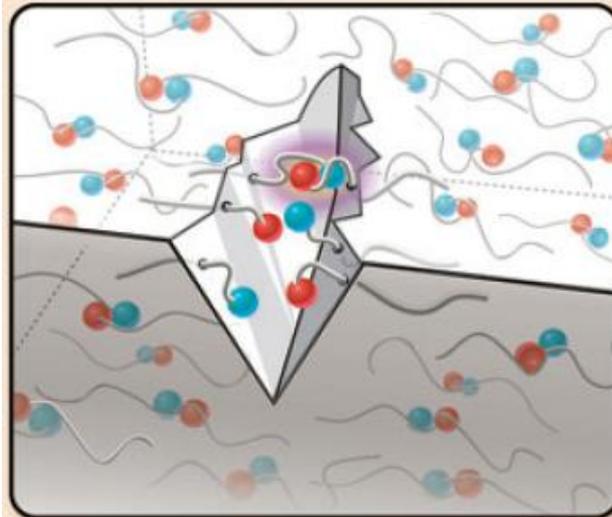
a Capsule based



b Vascular

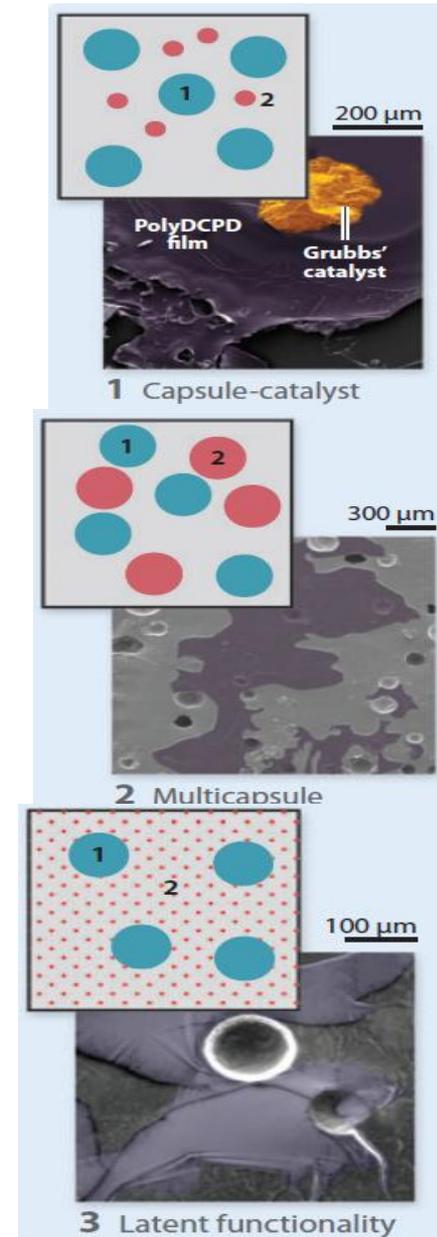
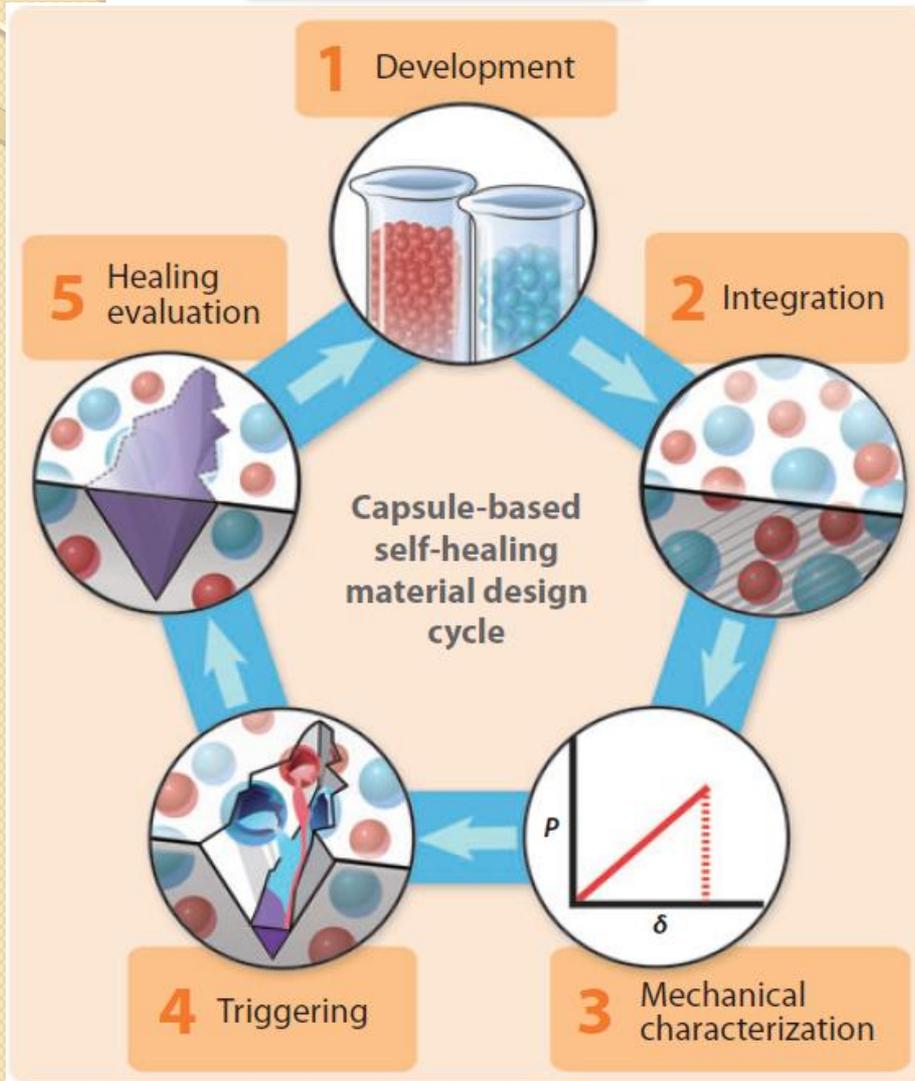


c Intrinsic

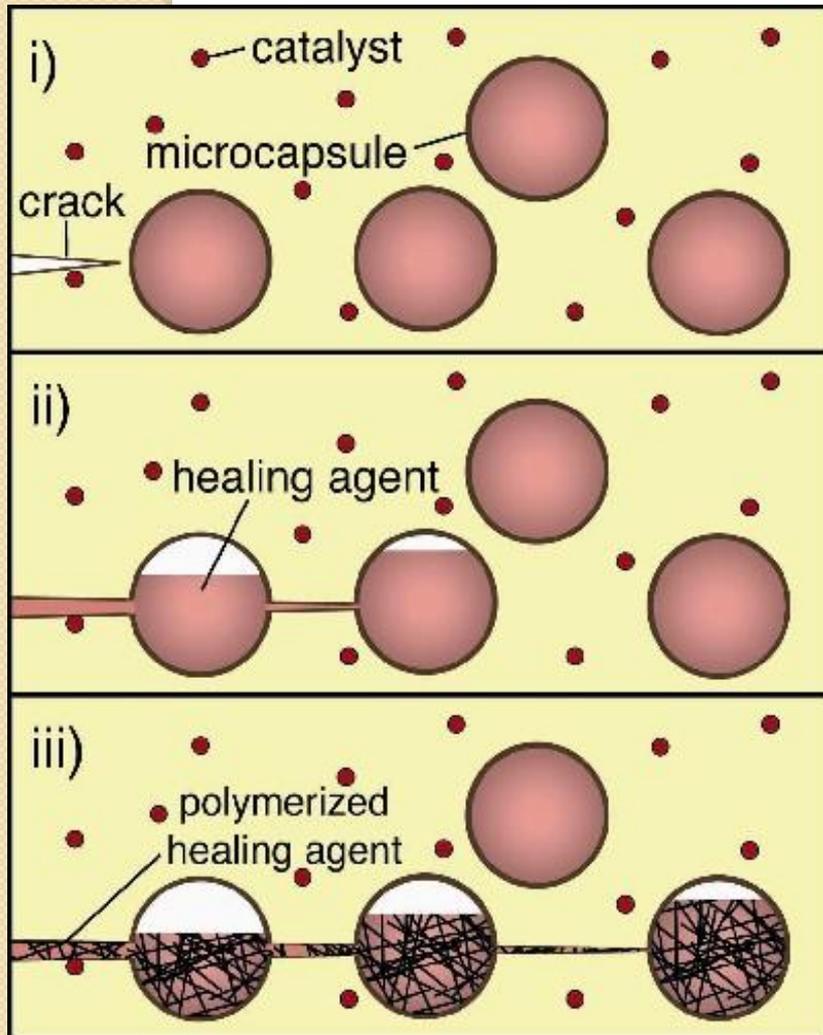


1 . Capsule-based Self-healing Material

Design cycle



Encapsulation-Type Self-Healing Materials



Skeme for autonomic healing of such type:

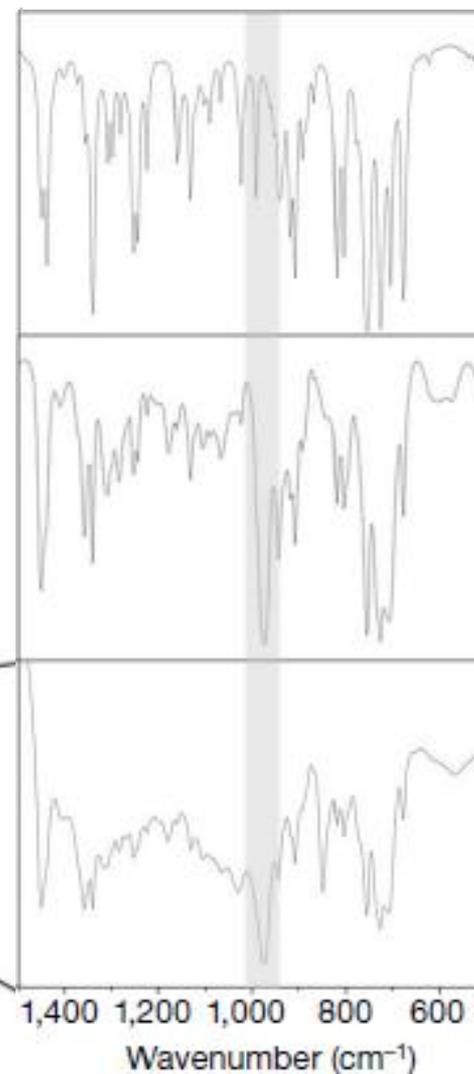
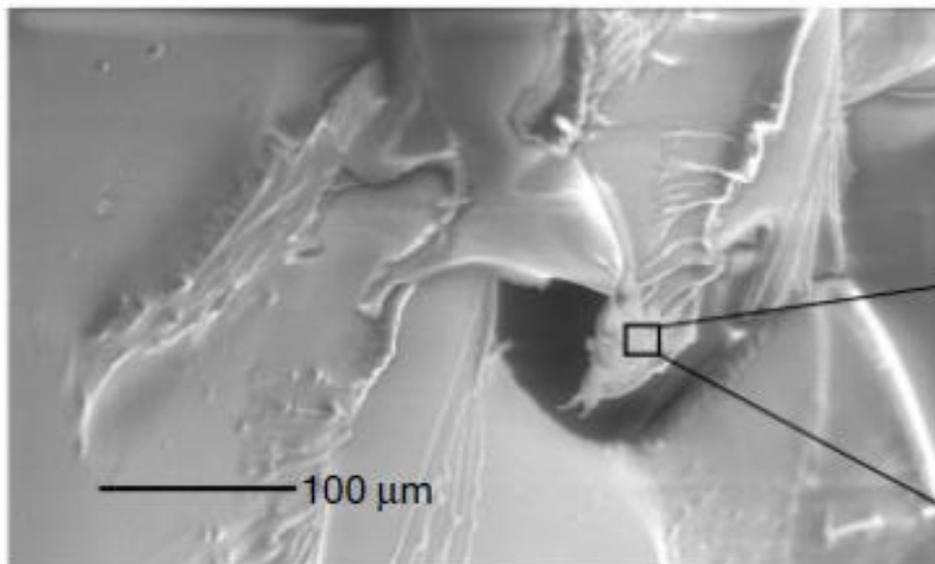
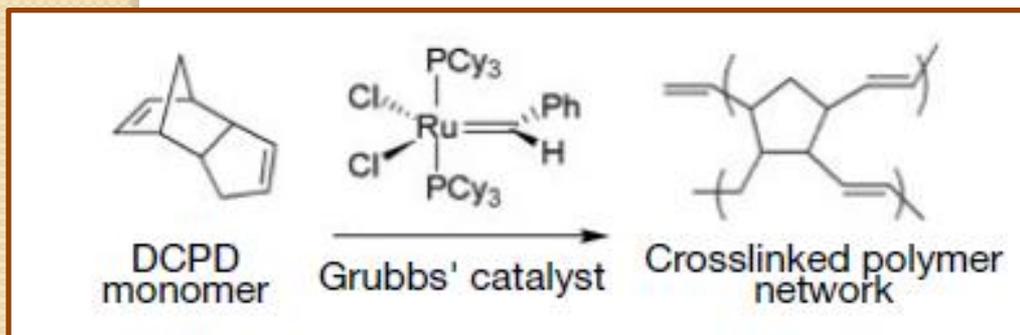
Damages trigger the release of healing reagent embedded in the matrix. Then polymerization proceeds under the act of catalyst contained in the matrix.

Self-healing processing stages:

- Cracks form in the matrix
- Crack propagation and rupture of microcapsules releasing healing reagent
- Crack-healing via polymerization of healing reagent

S.R. White *et al. Nature*, **2001**, 409, 794-797

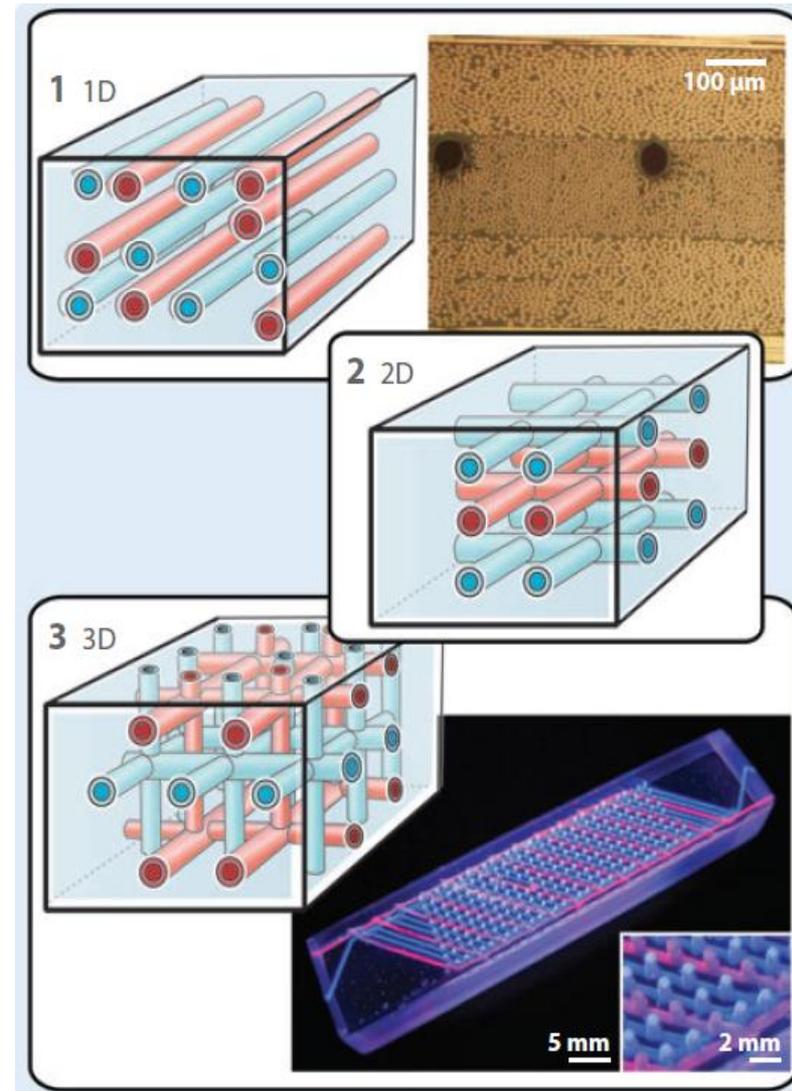
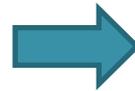
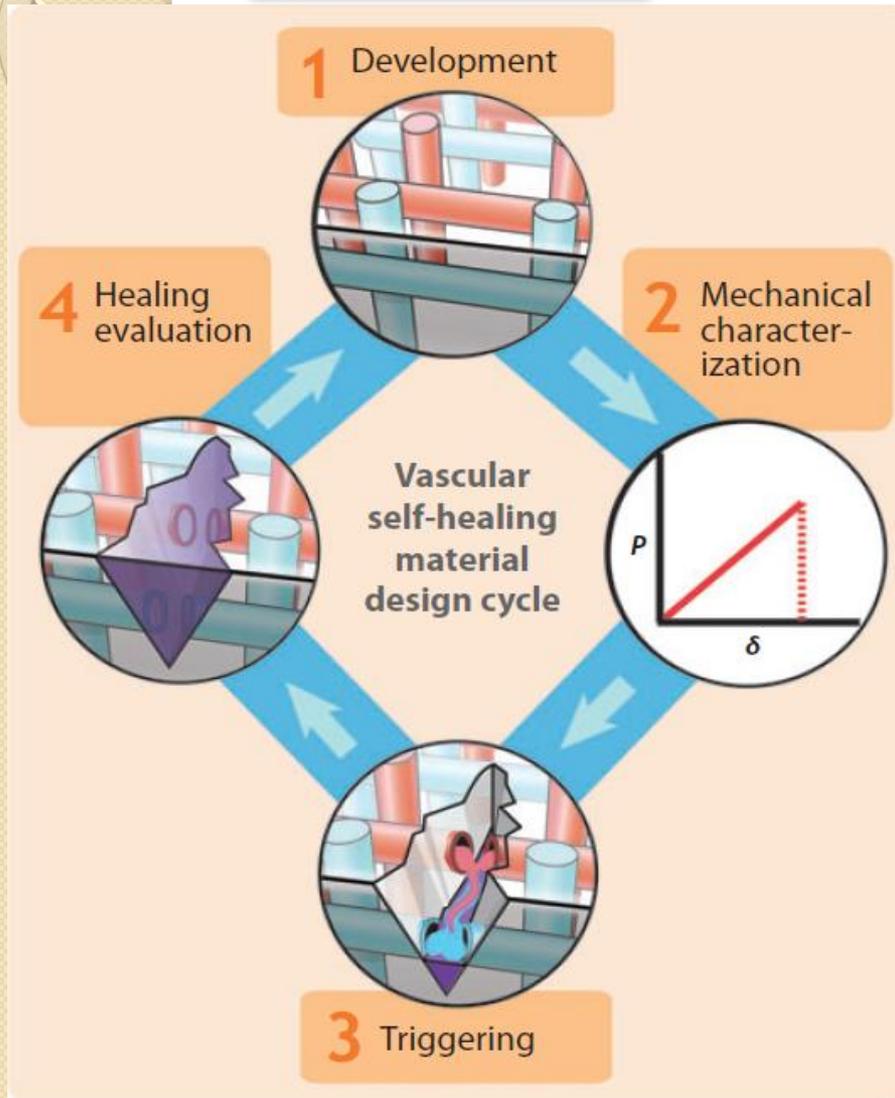
Basic Polymerization Reaction:



In this strategy, when catalyst and healing reagent is loaded by 2.5% and 10% (by weight), the average healing efficiency can reach up to 60% (max 75%).

2 . Microvascular Self-Healing Material

Design cycle



Microvascular-Type Self-Healing Materials

a

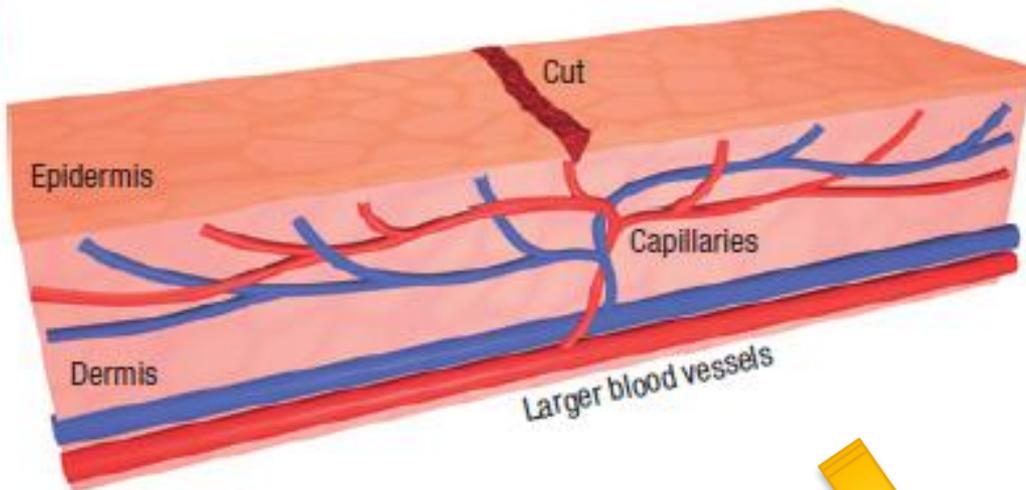
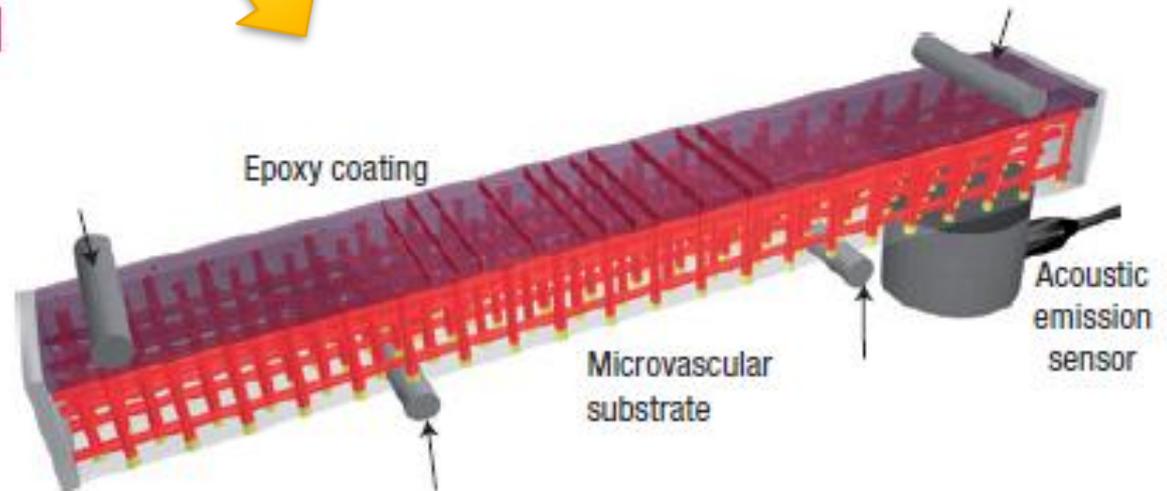


Image of skin with a cut in the epidermis layer

b



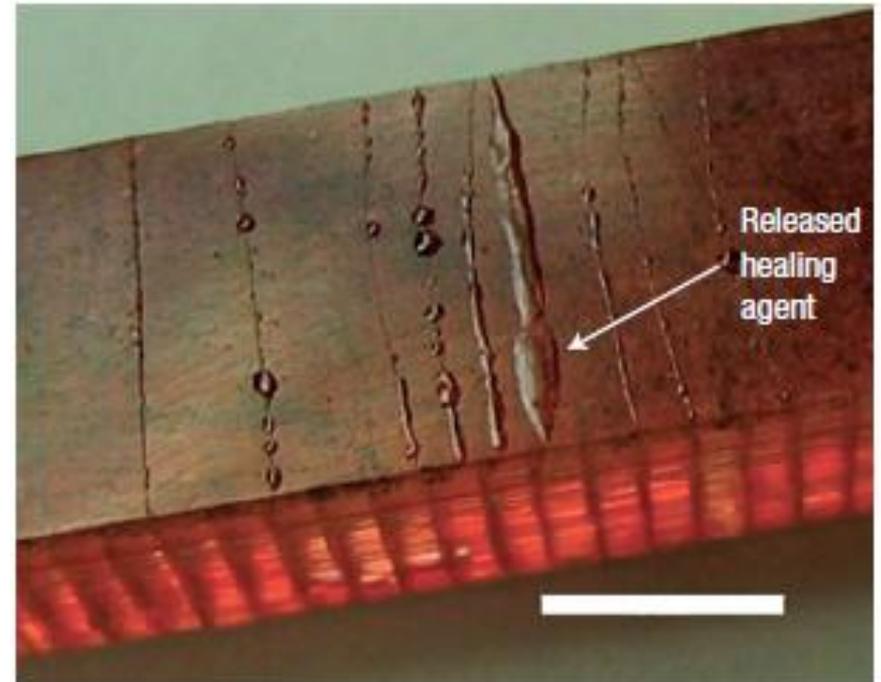
Schematic structure of a microvascular self-healing material

Skeme for self-healing of this type:

- ◆ Crack formation and attracted to more compliant region created by microvascules.
- ◆ Healing reagent wicks into crack(s) through capillary action.
- ◆ Polymerization begins once healing reagent interacts with catalyst coated on the surface.

Key points to the design:

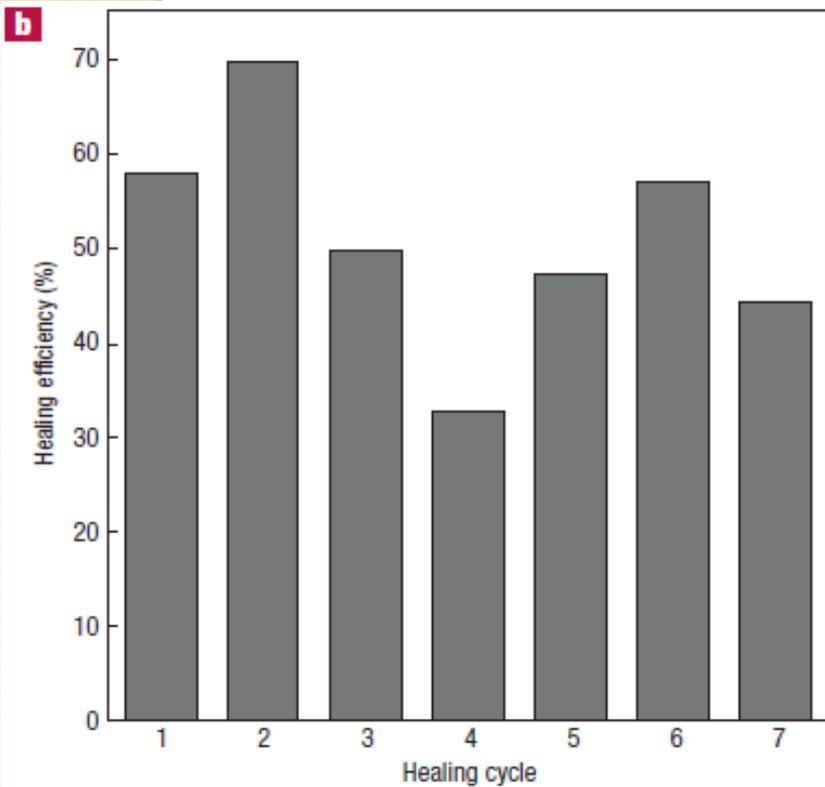
- Maximum channel spacing and minimum channel diameter.
- The channel diamete must be large enough for healing reagent to flow into the crack plane.



Cracks in coating

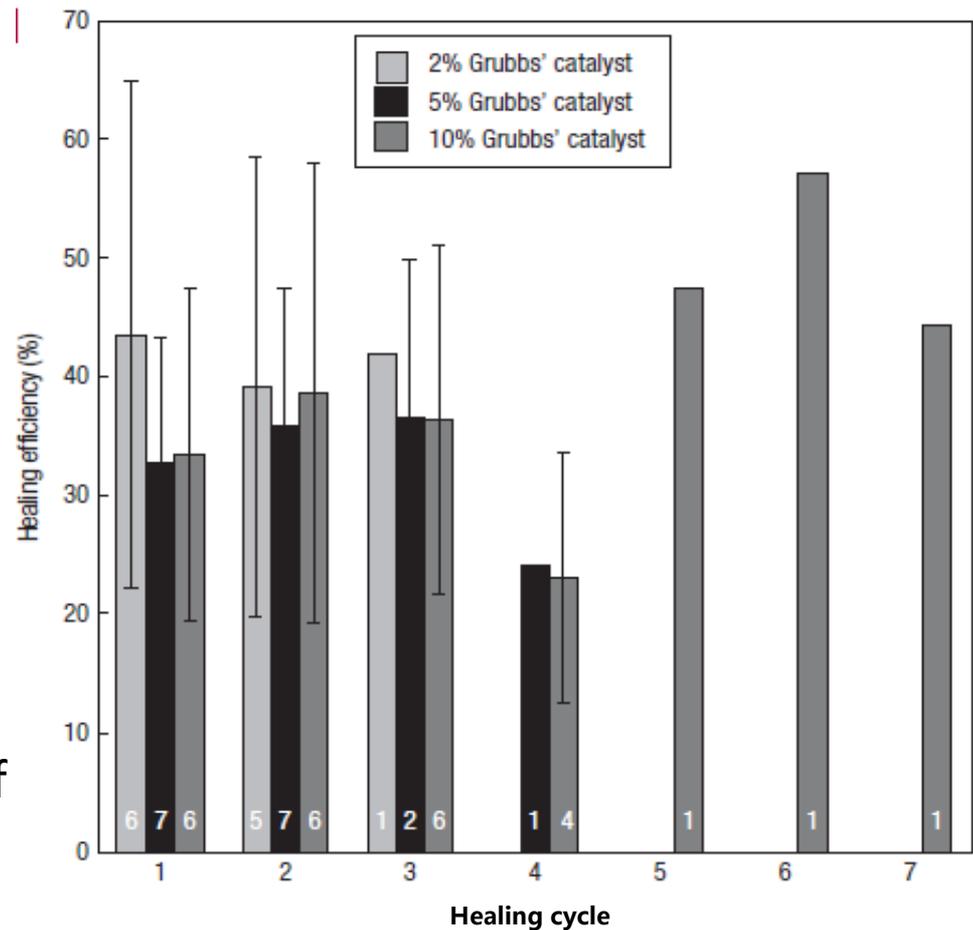
Microchannels

Released
healing
agent



- Healing reagent and catalyst are DCPD and Grubbs' catalyst, the same as first generation.

- Multi-time healing can be achieved due to refillable microvascular structure

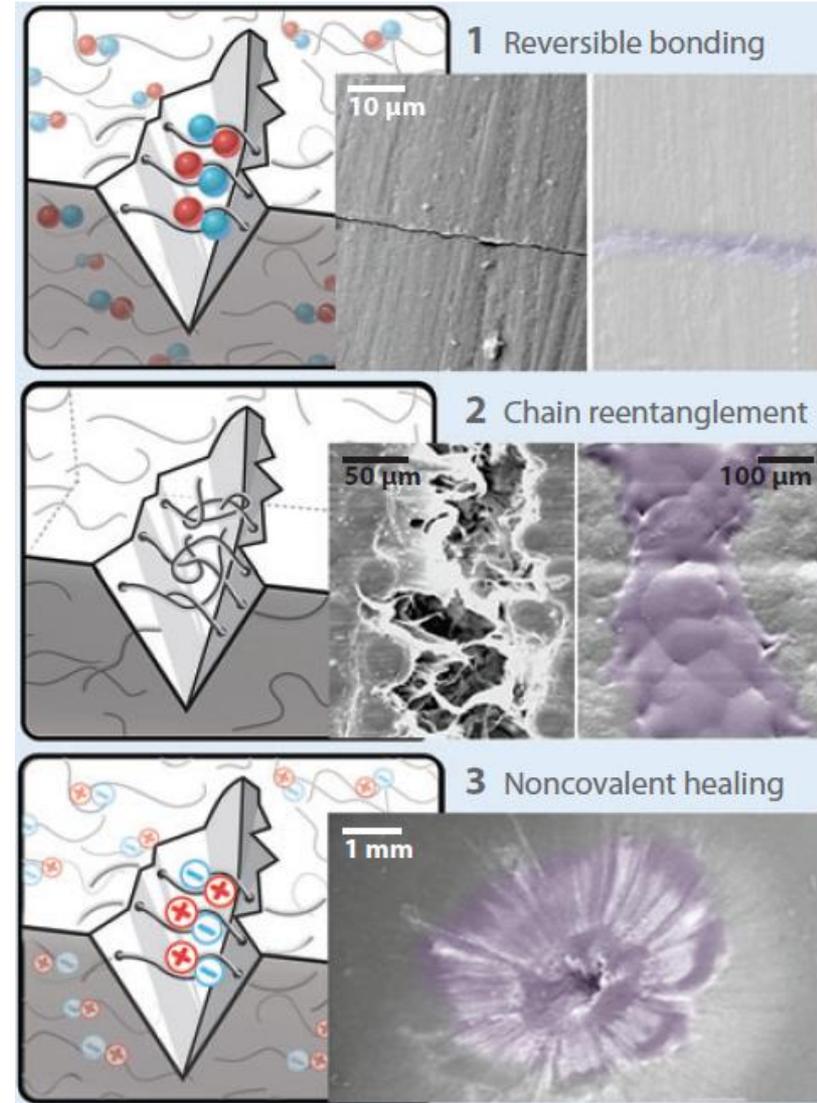
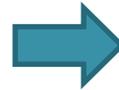
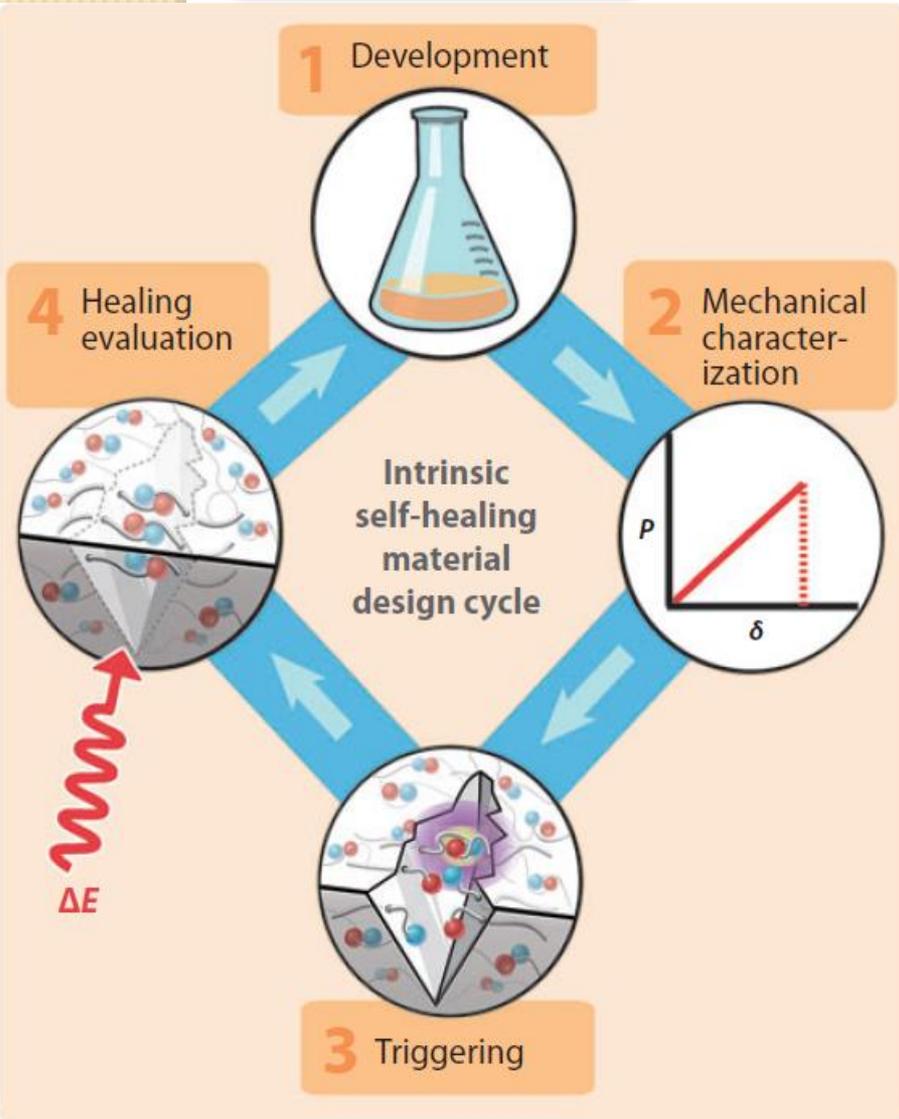


- Concentration of catalyst does not significantly influence the average healing efficiency.

- The loading amount of catalyst has great impact on the number of successful healing cycles achieved.

3 . Intrinsic Self-Healing Material

Design cycle



3-1. Reversible Covalent Bonding Approach

3-1-1 Employing thermally reversible DA cycloaddition

Basic polymerization reaction:

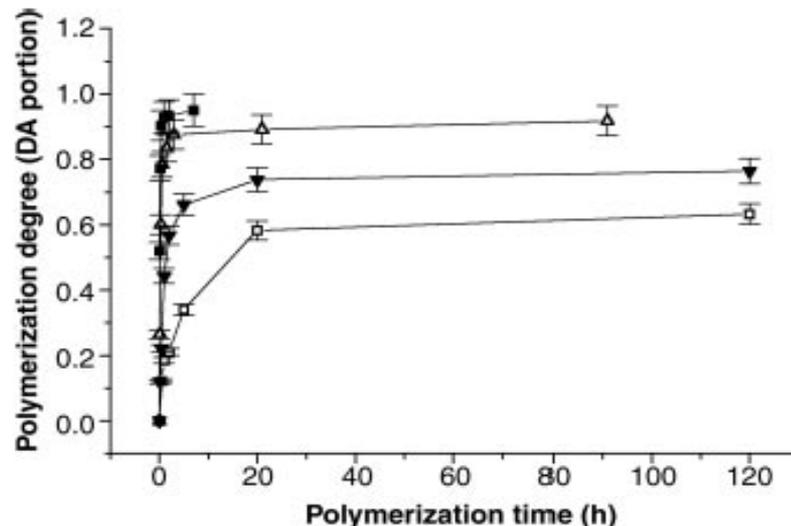
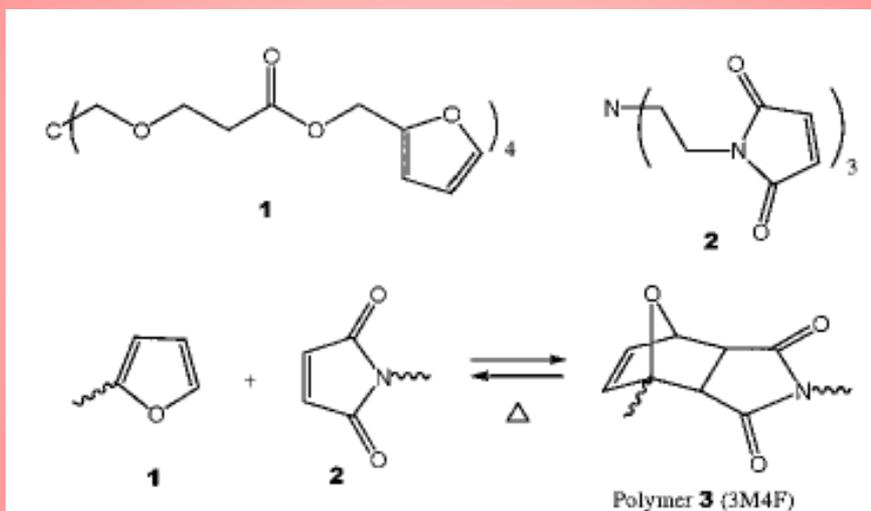


Fig. 1. Polymerization degree versus time. (□) 24°C; (▼) 45°C; (△) 60°C; (■) 75°C.

Characteristics of polymer 3:

- Easy to synthesize
- Having as good mechanical properties.
- Fully transparent

Properties	Polymer 3	Epoxy resins	Unsat. poly.
Tensile			
Strength (MPa)	68*	27 to 88	4 to 88
Modulus (GPa)	—	2.4	2 to 4.4
Elongation (%)	1.6 to 4.7	3 to 6	<2.6
Compression			
Strength (MPa)	121*	102 to 170	88 to 204
Modulus (GPa)	3.1	3.4†	
Flexural			
Strength (MPa)	143*	88 to 143	58 to 156
Modulus (GPa)	—		3.4 to 4.2‡

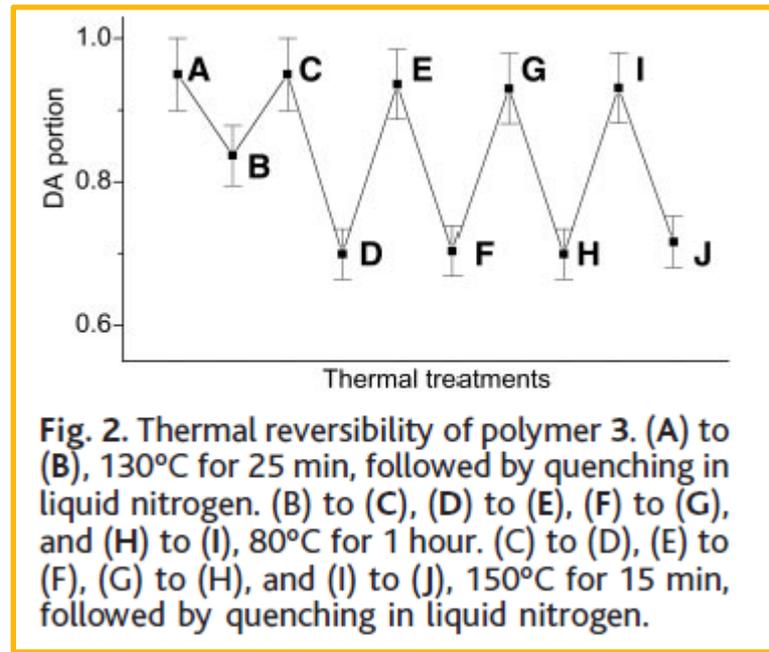
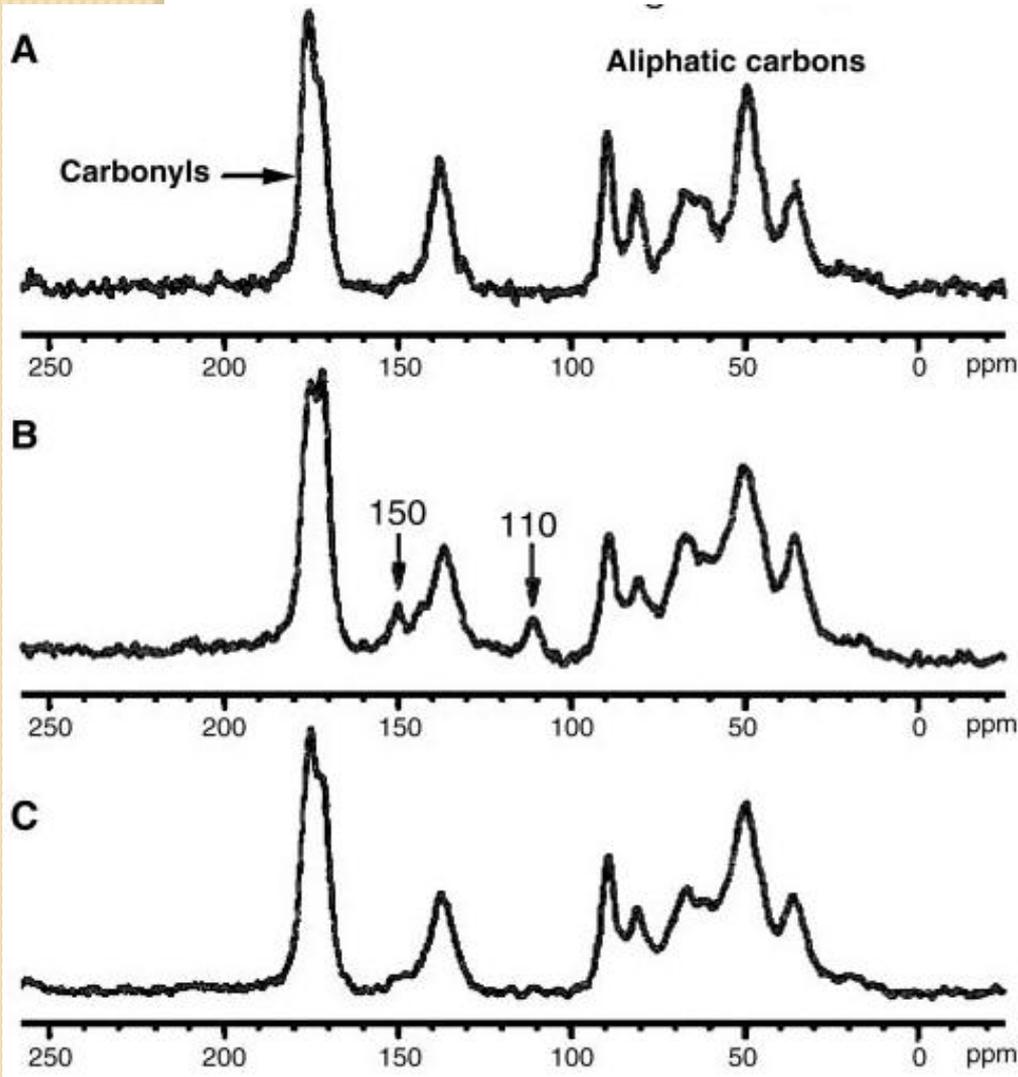
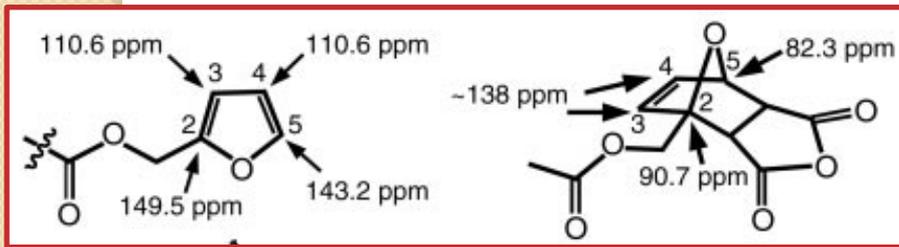
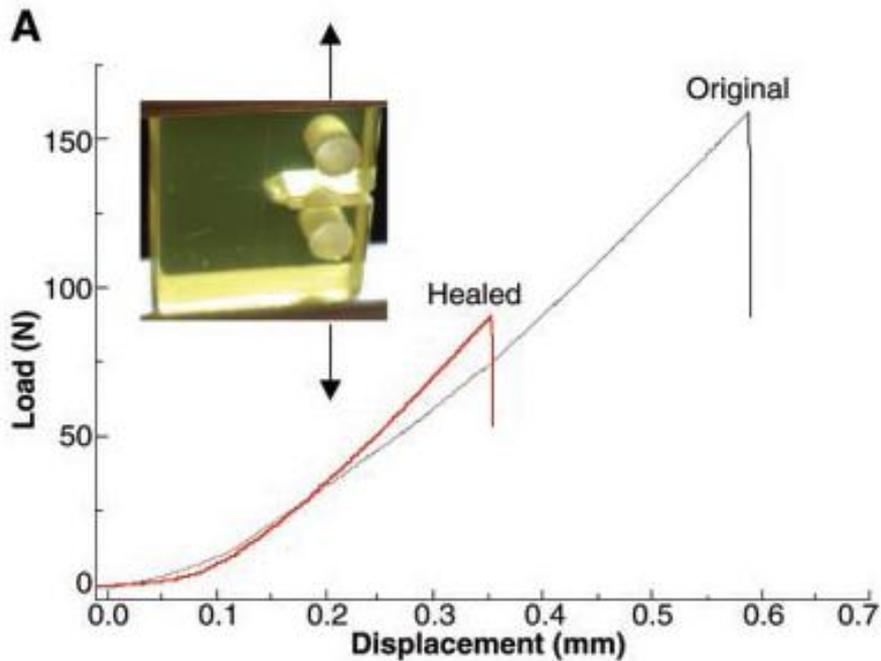


Fig. 2. Thermal reversibility of polymer 3. (A) to (B), 130°C for 25 min, followed by quenching in liquid nitrogen. (B) to (C), (D) to (E), (F) to (G), and (H) to (I), 80°C for 1 hour. (C) to (D), (E) to (F), (G) to (H), and (I) to (J), 150°C for 15 min, followed by quenching in liquid nitrogen.

(A) A fully polymerized sample

(B) A sample heated to 145°C and then quenched in liquid nitrogen

(C) A repolymerized sample (cooled from 120°C to 70°C in 24h)

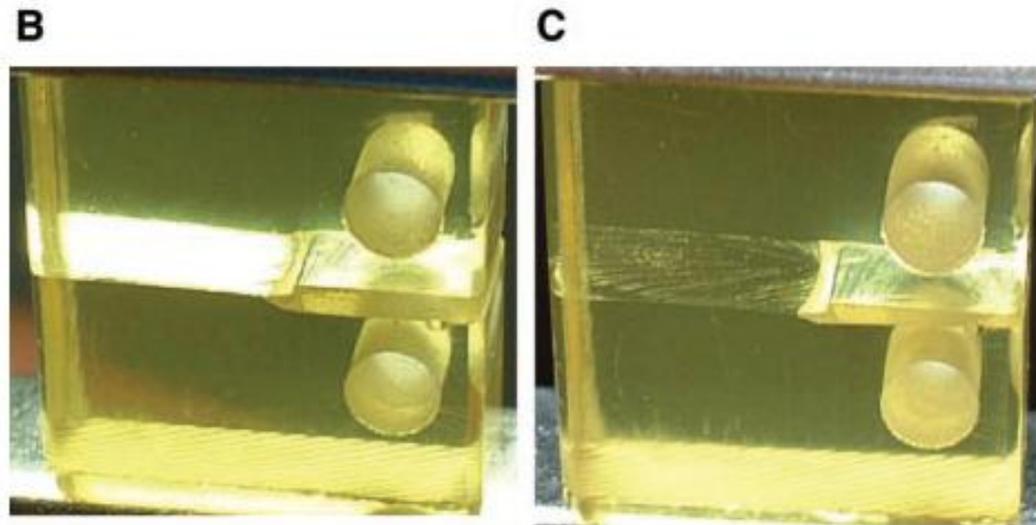


Pros and cons of this material system

- First report for self-healing material via reversible covalent bonding
- Multi-time healing can be achieved
- Good mechanical and optical properties
- × Relatively long curing time
- × Heating above 120°C is required for healing.

Fig. (A) Healing efficiency obtained by fracture toughness testing.

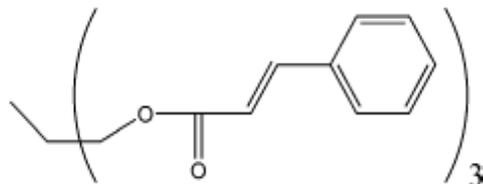
Fig. (B)/(C) A broken specimen before and after thermal treatment (120C to 150C under nitrogen for 2h then cooled to r.t.).



3-1-2. Employing Photochemical [2+2] Cycloaddition

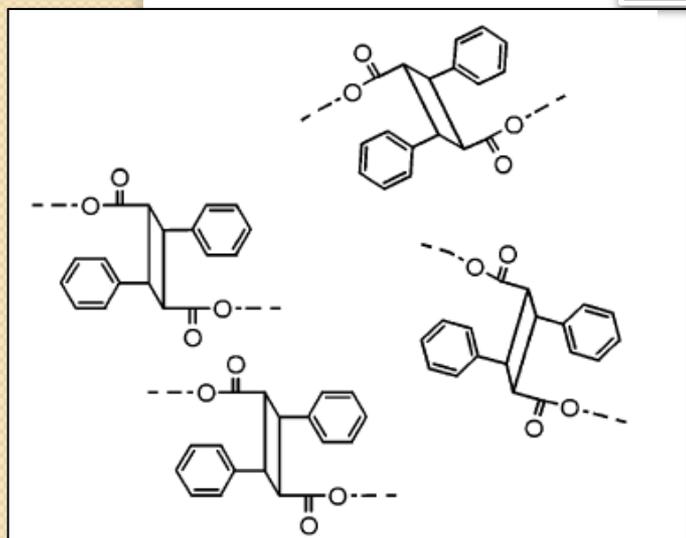
Characteristics of this material system

- Both TCE and TCE contained polymer can be easily prepared.
- Healing can be achieved by UV radiation (>280nm)
- Healing time is very short (2~10min) and multi-time healing is possible.



1,1,1-tris(cinnamoyloxymethyl)ethane
(TCE)

Working scheme



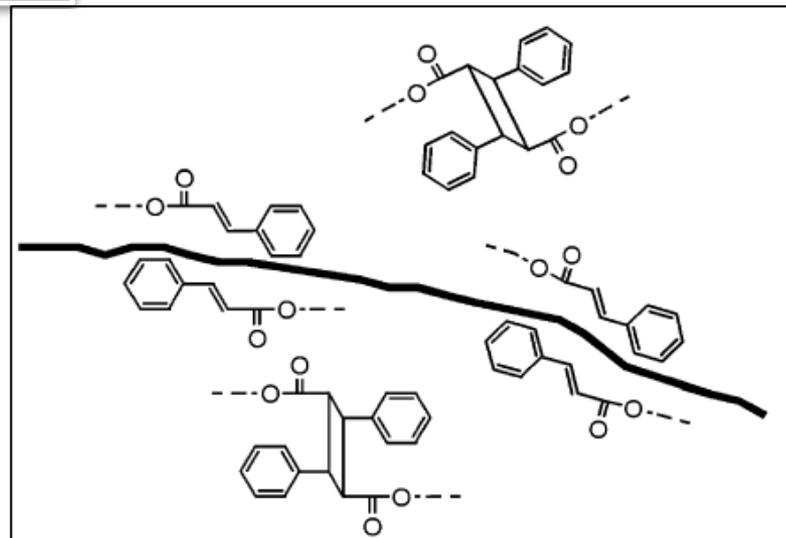
Crack formation



$h\nu$
(>280nm)



Healing



IR spectra of samples in range between 1600~1800 cm^{-1}

(a) TCE before irradiation (b) TCE after irradiation for 120s

(c) Polymer after grinding

(d) Grinded polymer after irradiation for 120s

Typical peaks: 1734 cm^{-1} for C=O in polymer
 1713 cm^{-1} for C=O in TCE monomer
 1637 cm^{-1} for C=C in TCE monomer

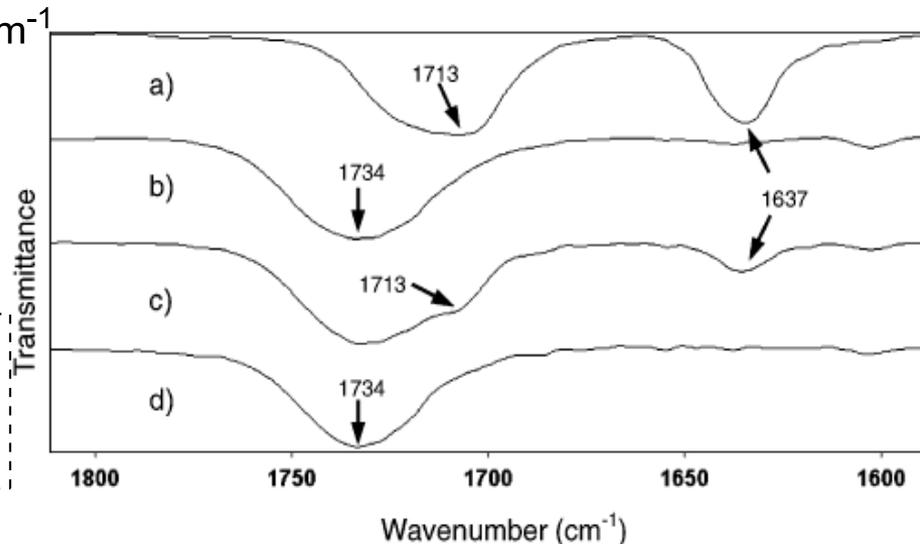


Table 1. Flexural Strength and Recovery of TCE-Derived Polymer Specimens

code ^b	UDMA/ TEGDMA (wt %)	TCE (wt %)	Flexural Strength (MPa) ^a			recovery (healed – cracked) (MPa)
			original	cracked	healed	
T40-H	60	40	42.1	3.1	3.2	0.1
T40-P	60	40	42.1	3.1	5.8	2.7
T40-PH	60	40	42.1	3.1	10.9	7.8
T30-PH	70	30	44.3	3.0	9.4	6.4
T20-PH	80	20	45.7	2.9	5.4	2.5
T10-PH	90	10	48.7	3.4	4.9	1.5
T0-PH	100	0	49.6	3.2	3.1	-0.1

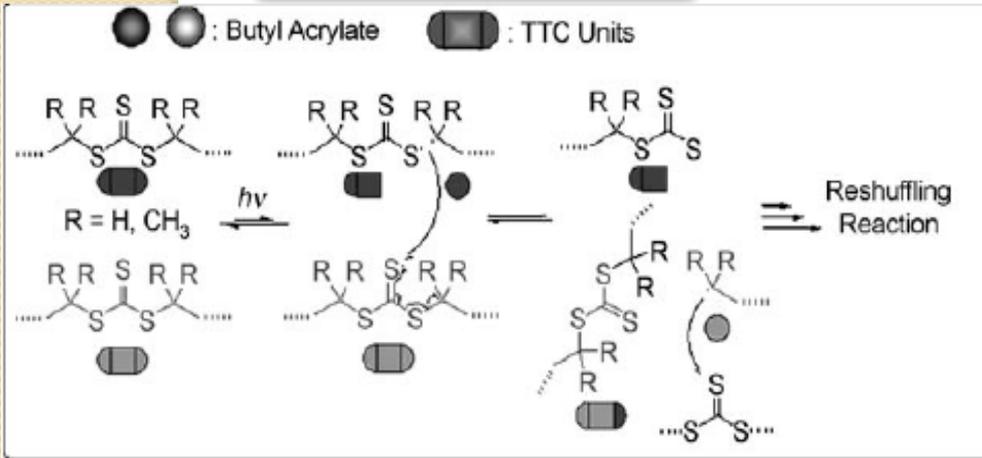
◆ Just heating or without TCE, healing did not proceed.

◆ Combination of irradiation and heating can give higher healing efficiency.

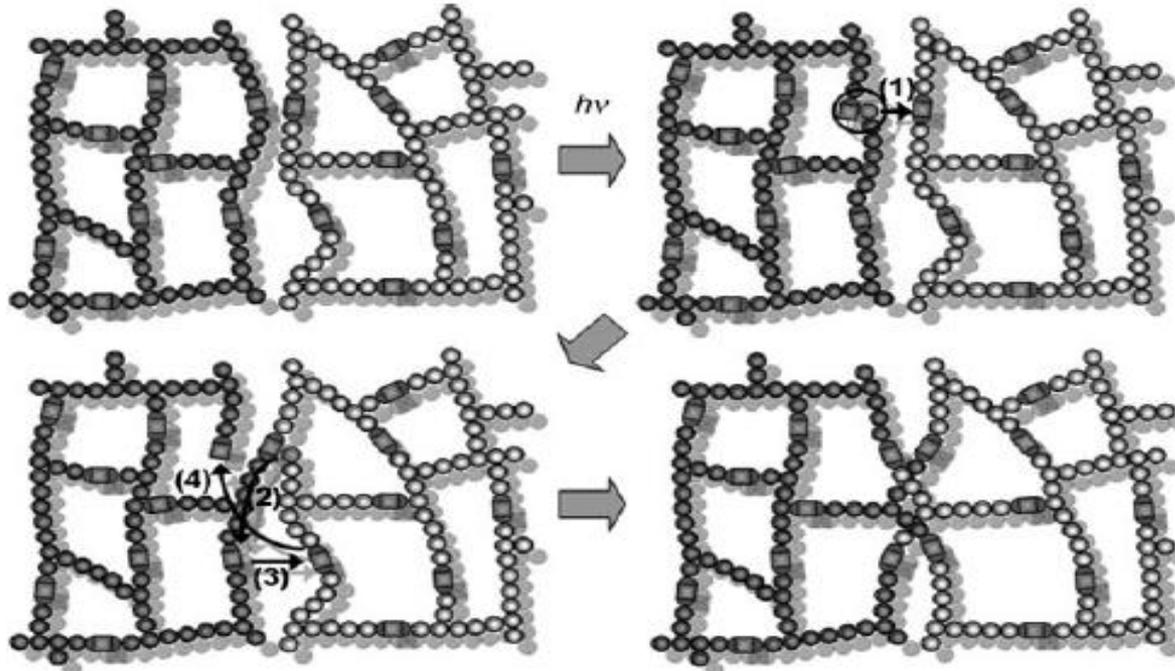
◆ Overall healing efficiency for this system is low.

3-1-3. Photo-induced Self-healing through Reshuffling of Trithiocarbonate

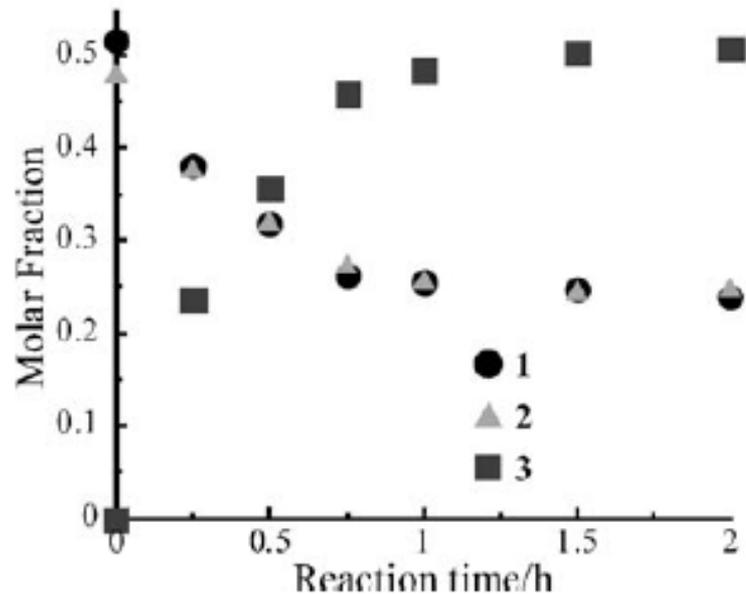
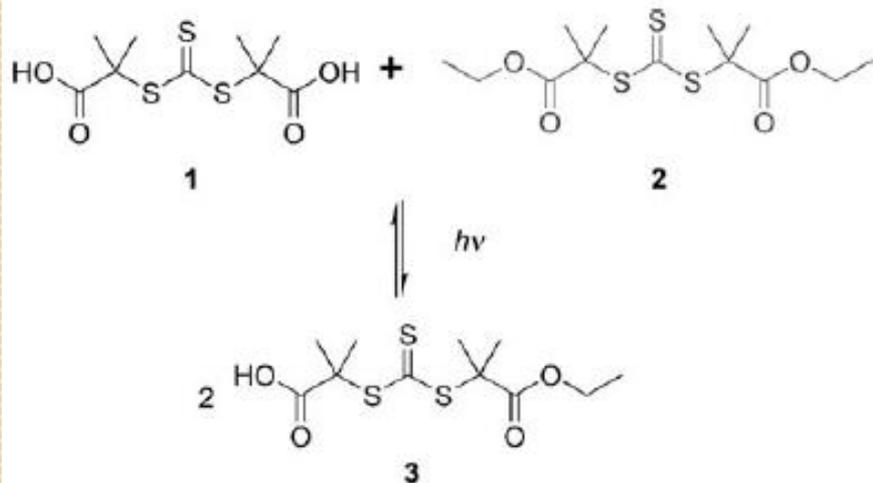
Working scheme



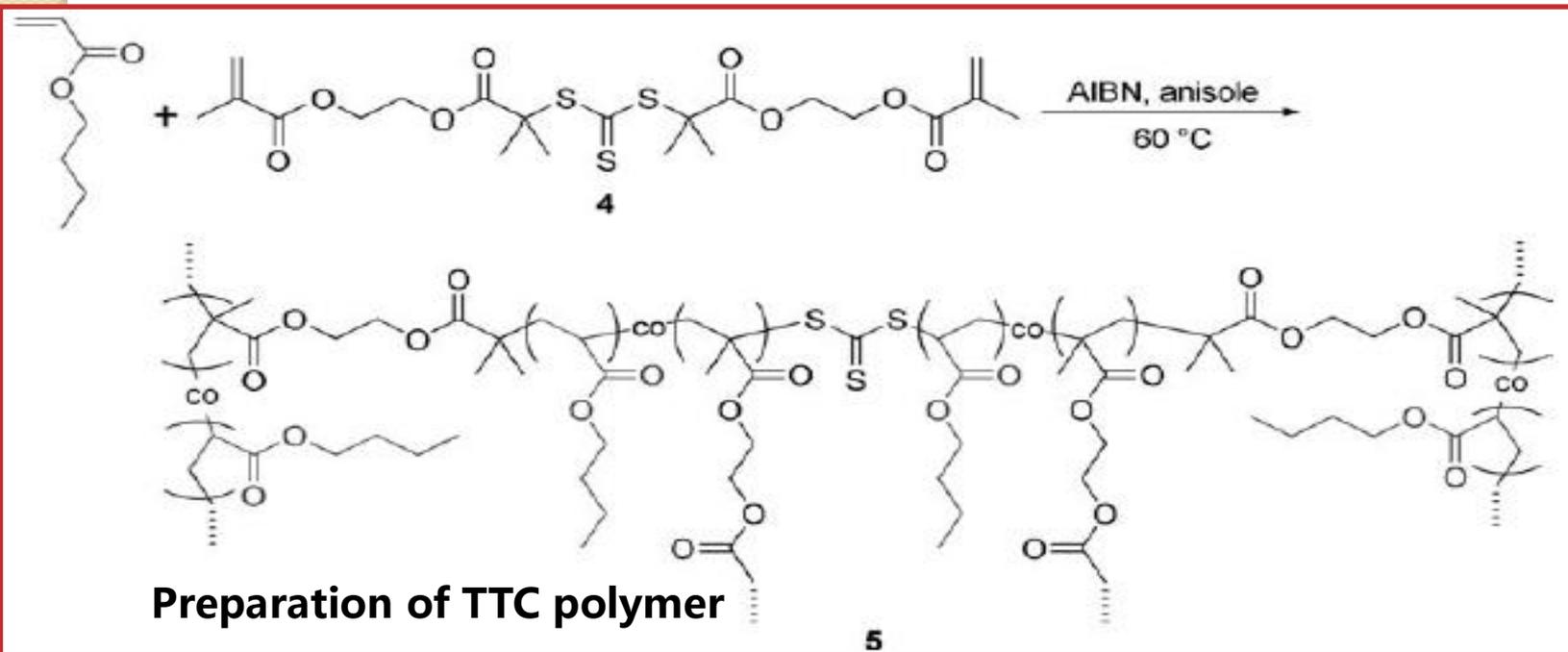
First example that achieves both a repeatable self-healing through **photo-induced covalent crosslink formation** and **macroscopic fusion of separate pieces** simultaneously.

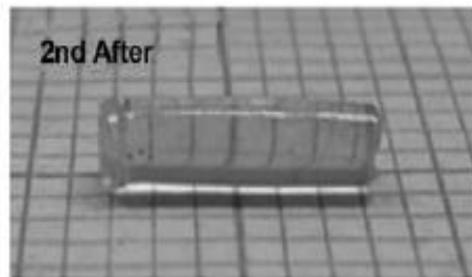
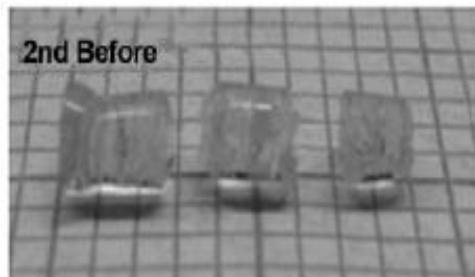
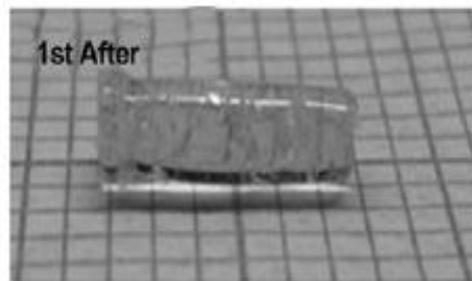
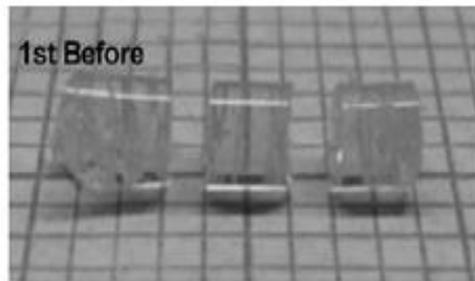


Model reaction



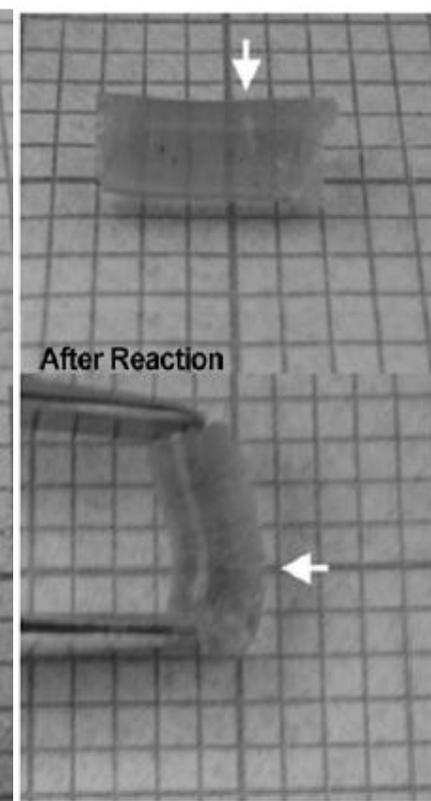
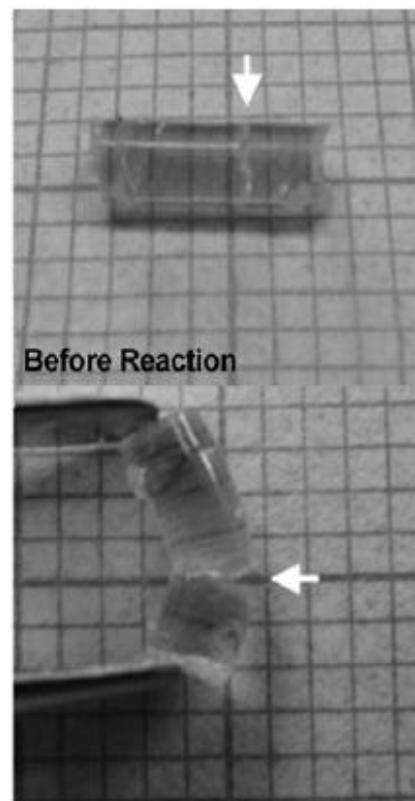
*MeCN, 0.04M, UV irradiation at r.t.





(A) Repetitive self-healing rxns under UV in MeCN

(B) Bulk state self-healing experiments for 48h

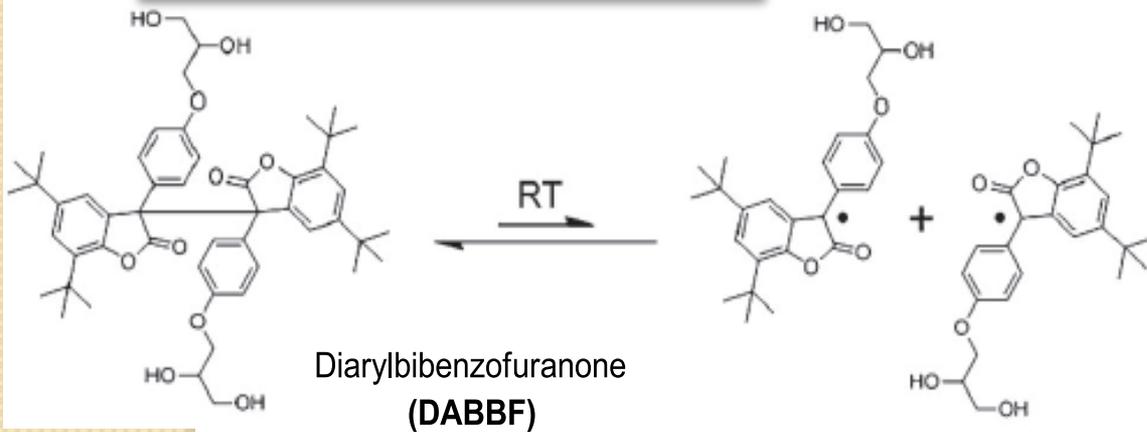


Characteristics of this system

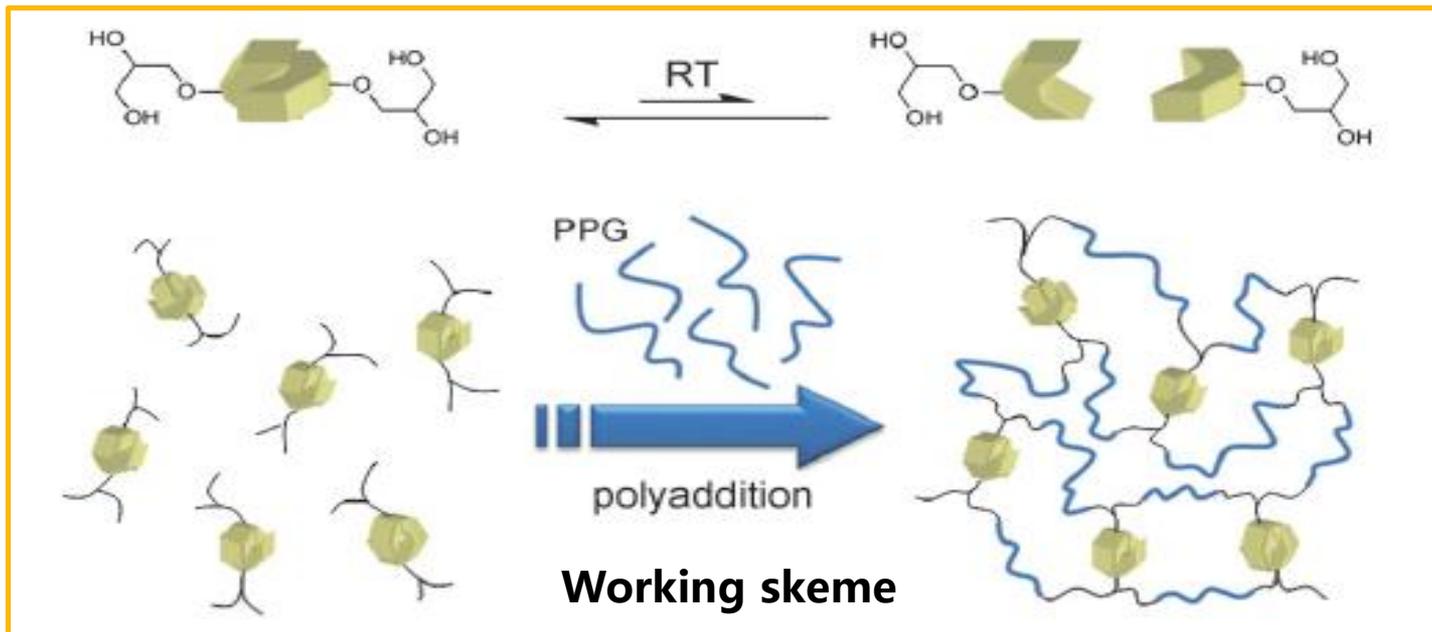
- Healing can be achieved just by UV irradiation under r.t.
- First report of macroscopic fusion through photoinduced covalent bond formation.
- Multi-time healing with high healing efficiency is possible.

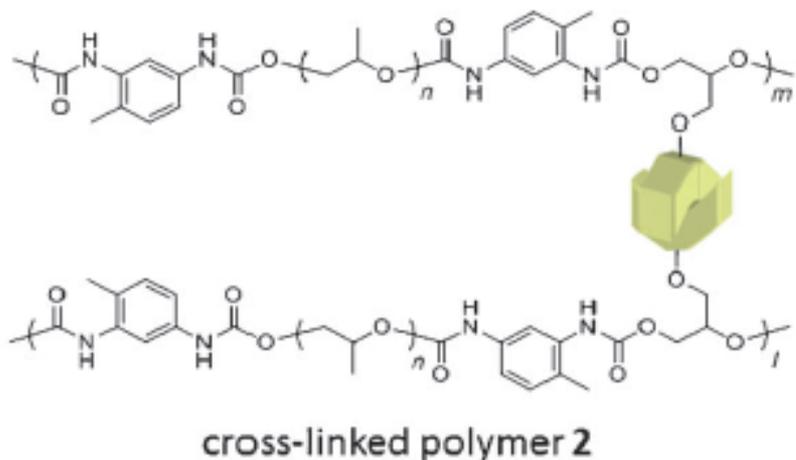
3-1-4. Self-healing through trigger-free radical-derived dynamic covalent bond

Characteristics of DABBF

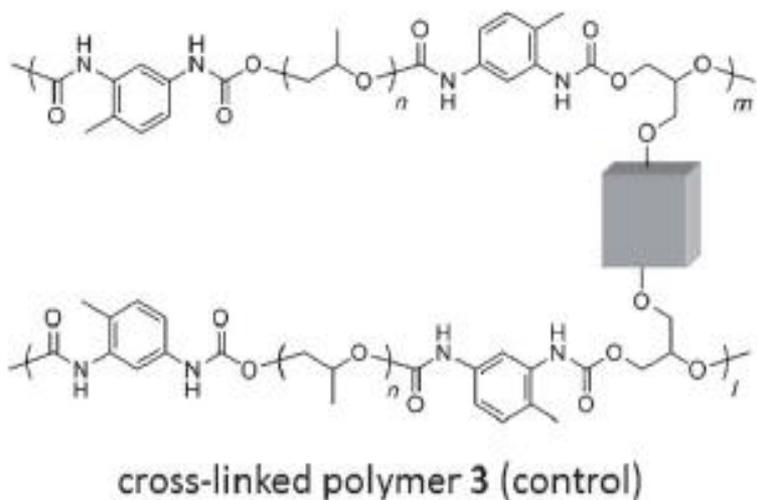
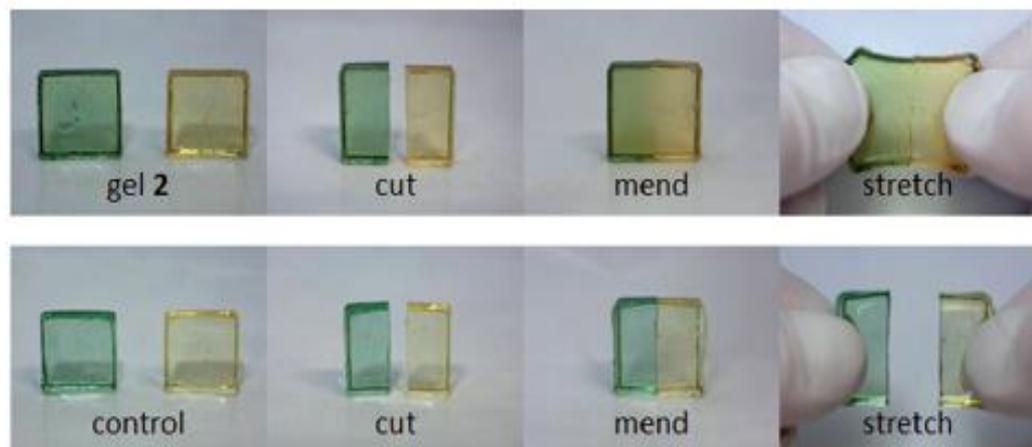


- Can reach a thermodynamic equilibrium under r.t. without special stimuli.
- Its radical species is O₂ tolerant.

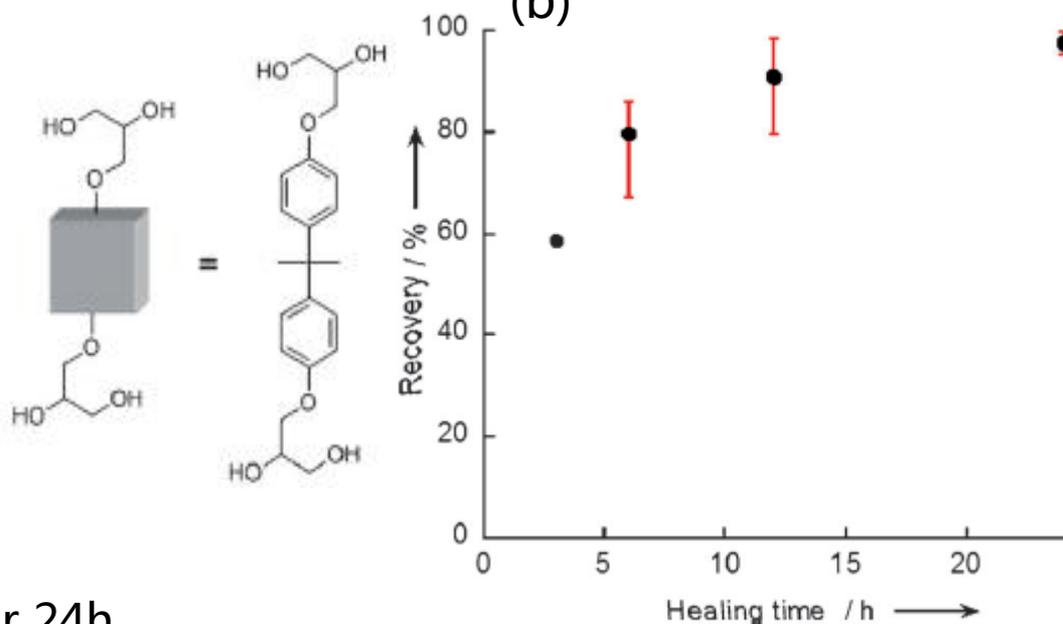




(a)



(b)



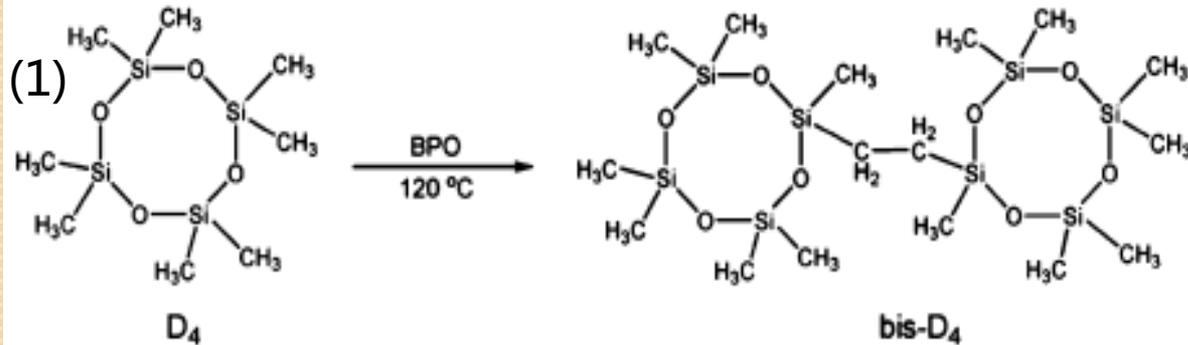
(a) Healing exp. at r.t. under air for 24h.

(b) Stress-strain curves of mended polymer over time. (3 samples)

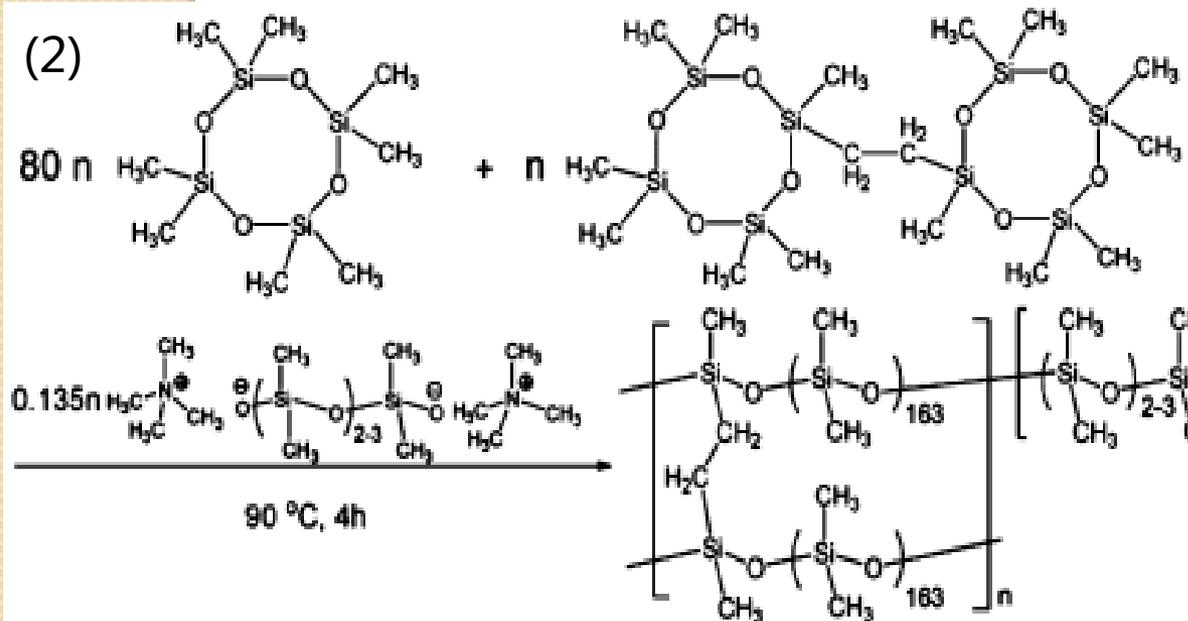
A. Takahara, H. Otsuka, *ACIE*, **2012**, *51*, 1138-1142

3-1-5. Self healing through anionic siloxane equilibration

Synthesis of this siloxane system



(1) BPO derived oxidative coupling of Octamethyl cyclotetrasiloxane(D4)

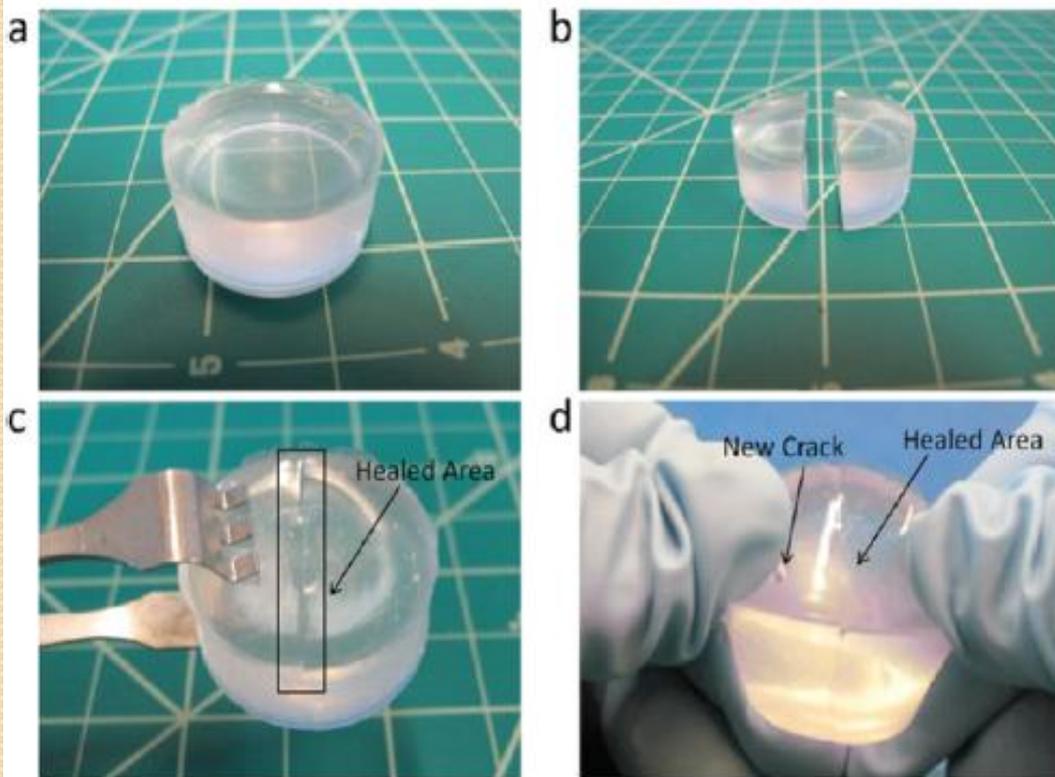


(2) Polymerization from D4 and bis-D4 under act of bis(tetramethylammonium)oligodimethylsiloxanediolate(BT AODMS).

* BTAODMS acts as anionic polymerization initiator.

* Bis-D4 plays as source of crosslinkings.

Healing experiment



- (a) Original cylindrical sample ($d=2.35\text{cm}$, $h=1\text{cm}$)
- (b) Sample cut into halves
- (c) Same sample 24h after healing at 90°C
- (d) The healed sample deformed by hand

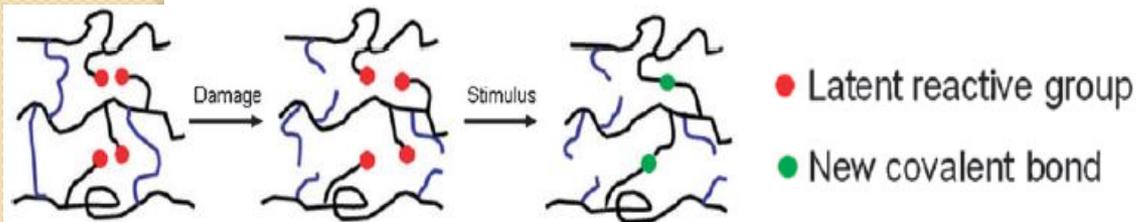


Characteristics of this system

- ◆ Easily accessible heating conditions (Heating around 90°C)
- ◆ Multi-time healing is possible with almost 100% recovery.
- ◆ The monomer is very cheap and innocuous.

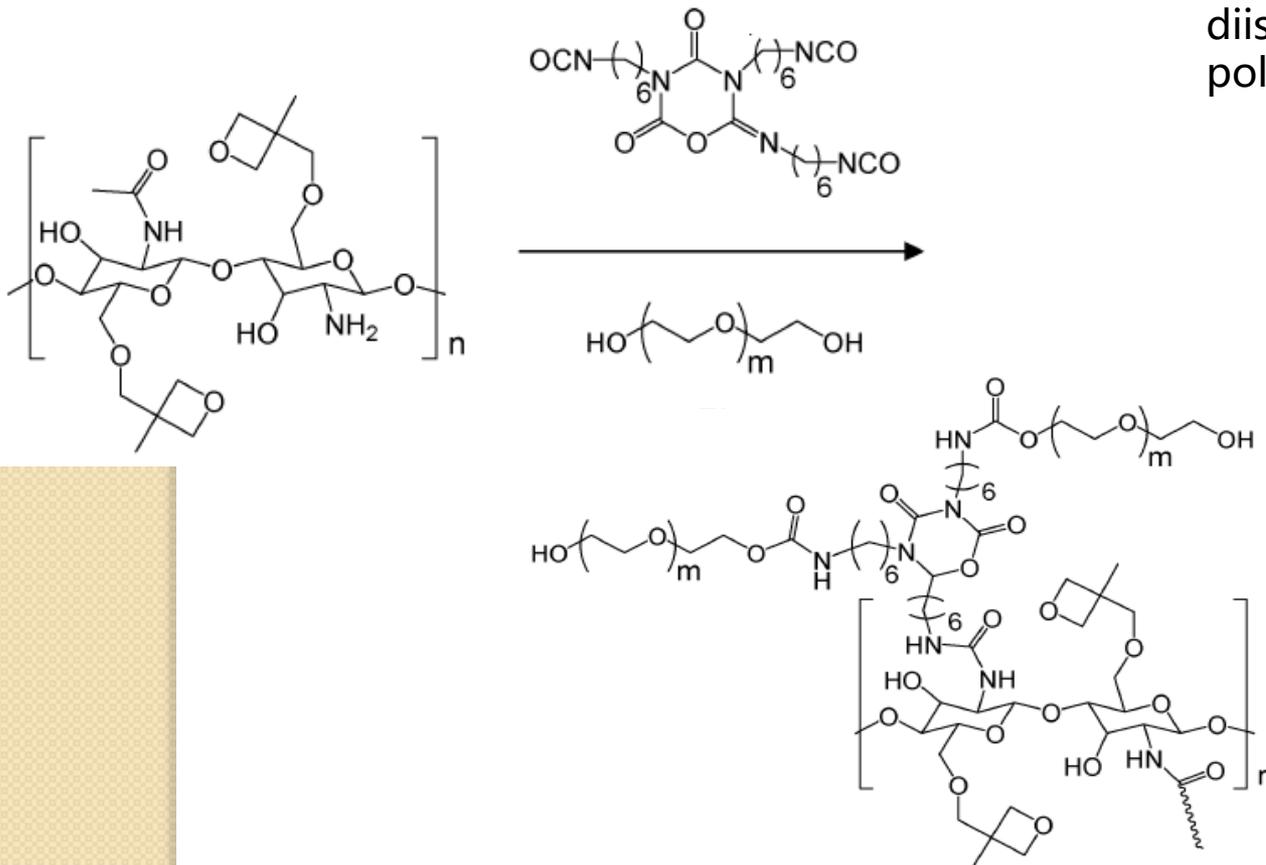
3-2. Chain Reentanglement Approach

Working skeme:



Basic polymerization reaction

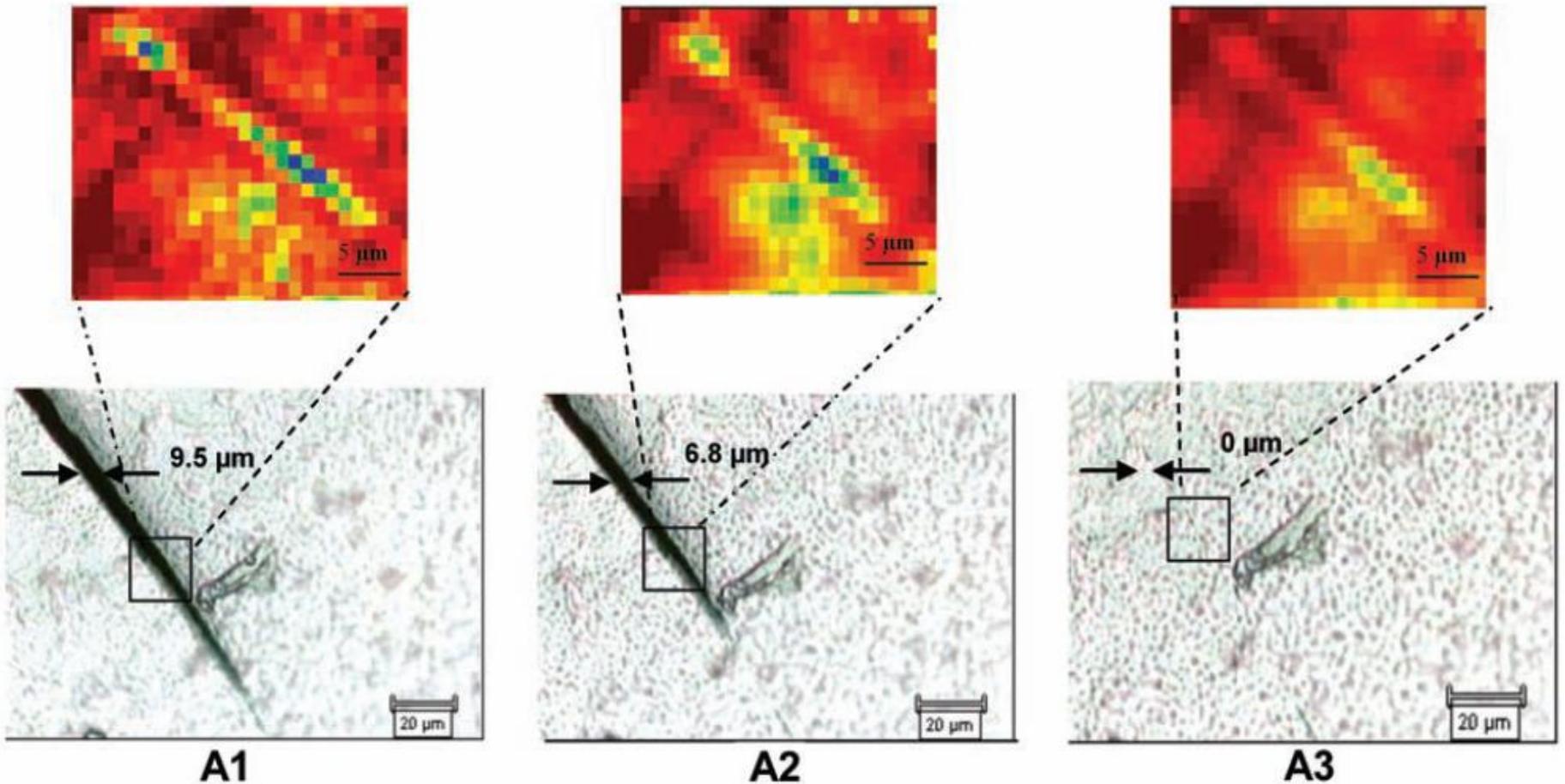
- (1) Introduction of oxetane(OXE) group to chitin(CHI)
- (2) Incorporation of OXE-CHI into trifunctional hexamethylene diisocyanate(HDI) in presence of polyethyleneglycol(PEG).



Working mechanism

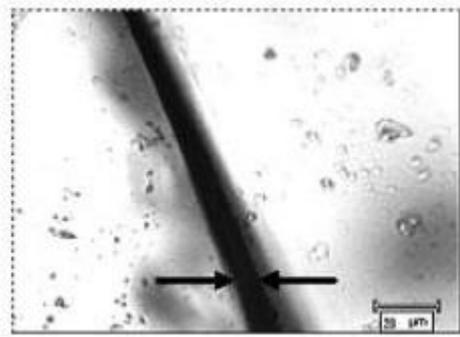
- (1) Upon mechanical damage of the network, oxetane rings open to create two reactive ends.
- (2) Chitin chain scission occurs when exposed to UV.
- (3) Above two kinds of reactive species form new crosslinks.

Healing experiment (I)

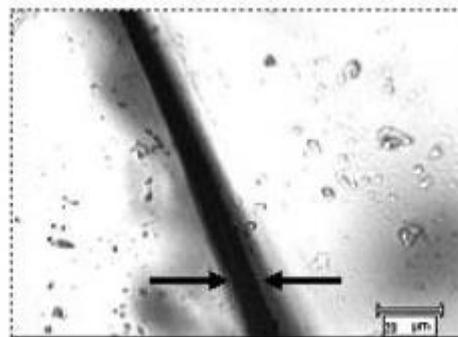


IR(upper) and optical(lower) images of OXE-CHI-PUR networks recorded as a UV exposure time. A1, 0 min; A2, 15 min; A3, 30 min by 120W fluorescent UV lamp at 302nm wavelength.

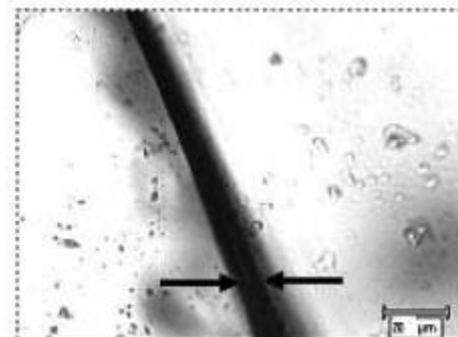
Healing experiment (II)



A1



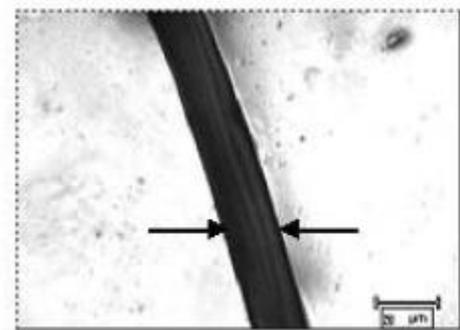
A2



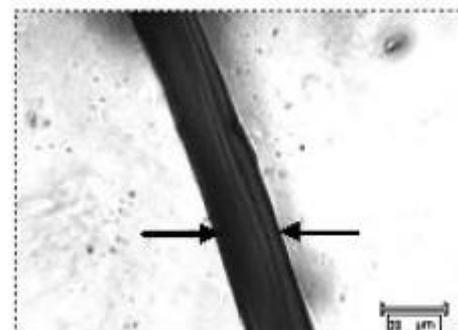
A3

(A) HDI:PEG:CHI =
1: 1.4: $0.57 \cdot 10^{-4}$

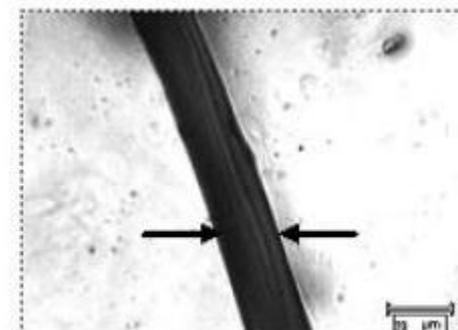
A1, 0 min; A2, 15
min; A3, 30 min to
UV irradiation



B1



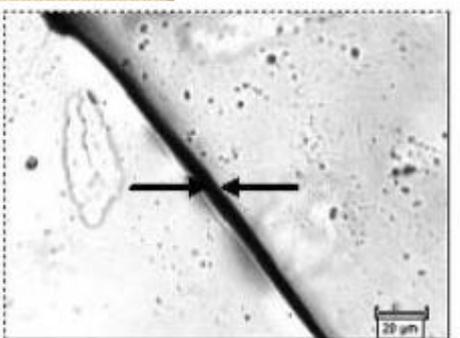
B2



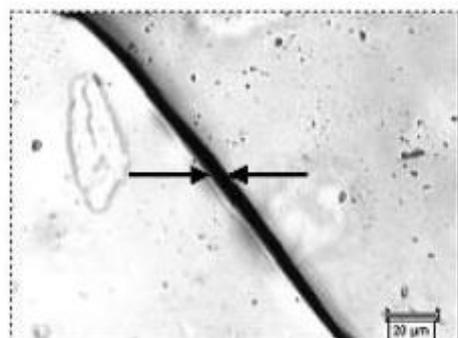
B3

(B) HDI:PEG:OXE-
CHI =
1: 1.4: $0.57 \cdot 10^{-4}$

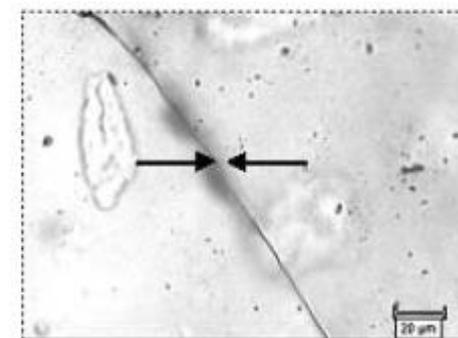
B1, 0 min; B2, 15
min; B3, 30 min
to UV irradiation



C1



C2



C3

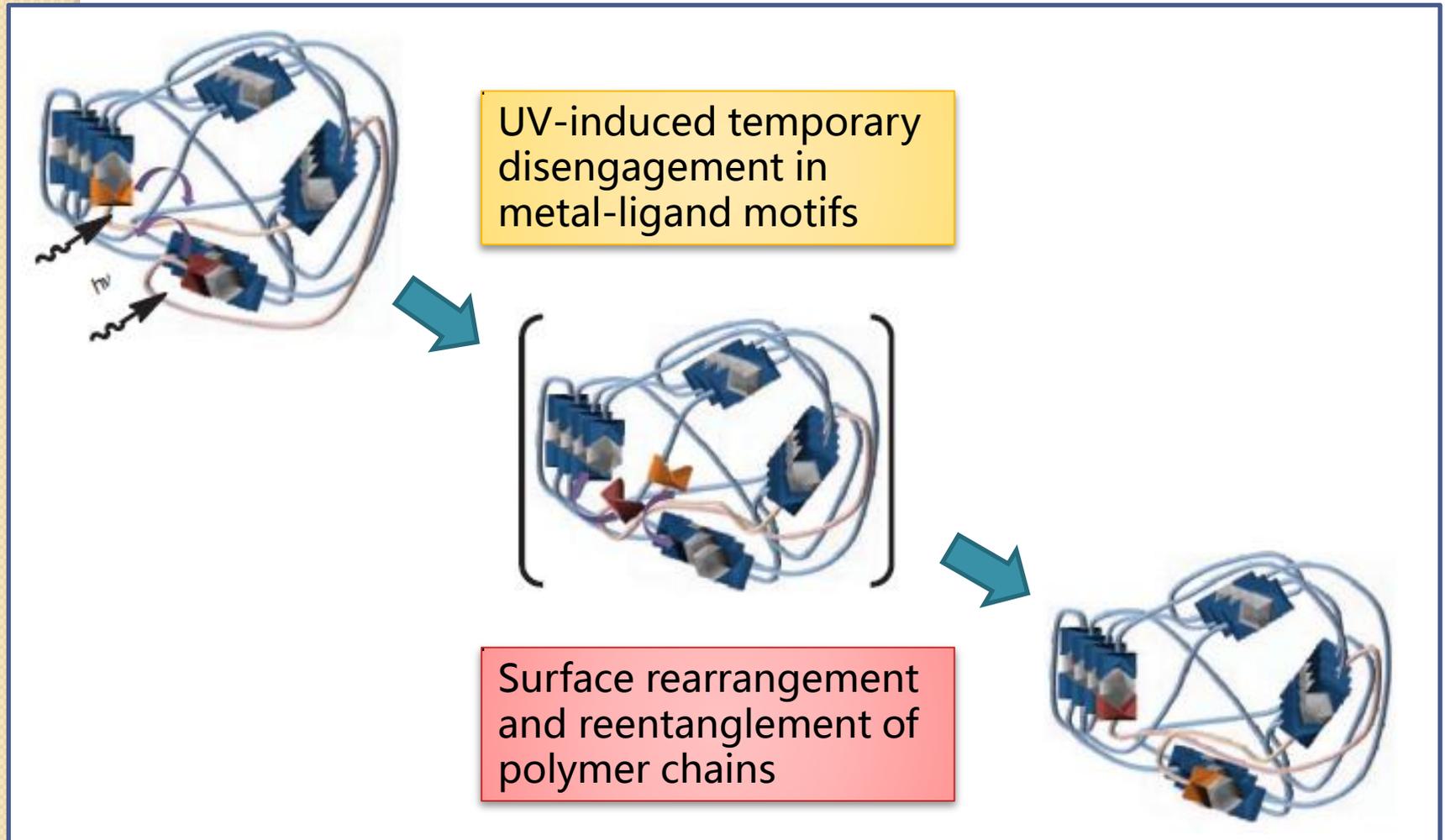
(C) HDI:PEG:OXE-
CHI =
1: 1.33: $1.17 \cdot 10^{-4}$

C1, 0 min; C2, 15
min; C3, 30 min to
UV irradiation

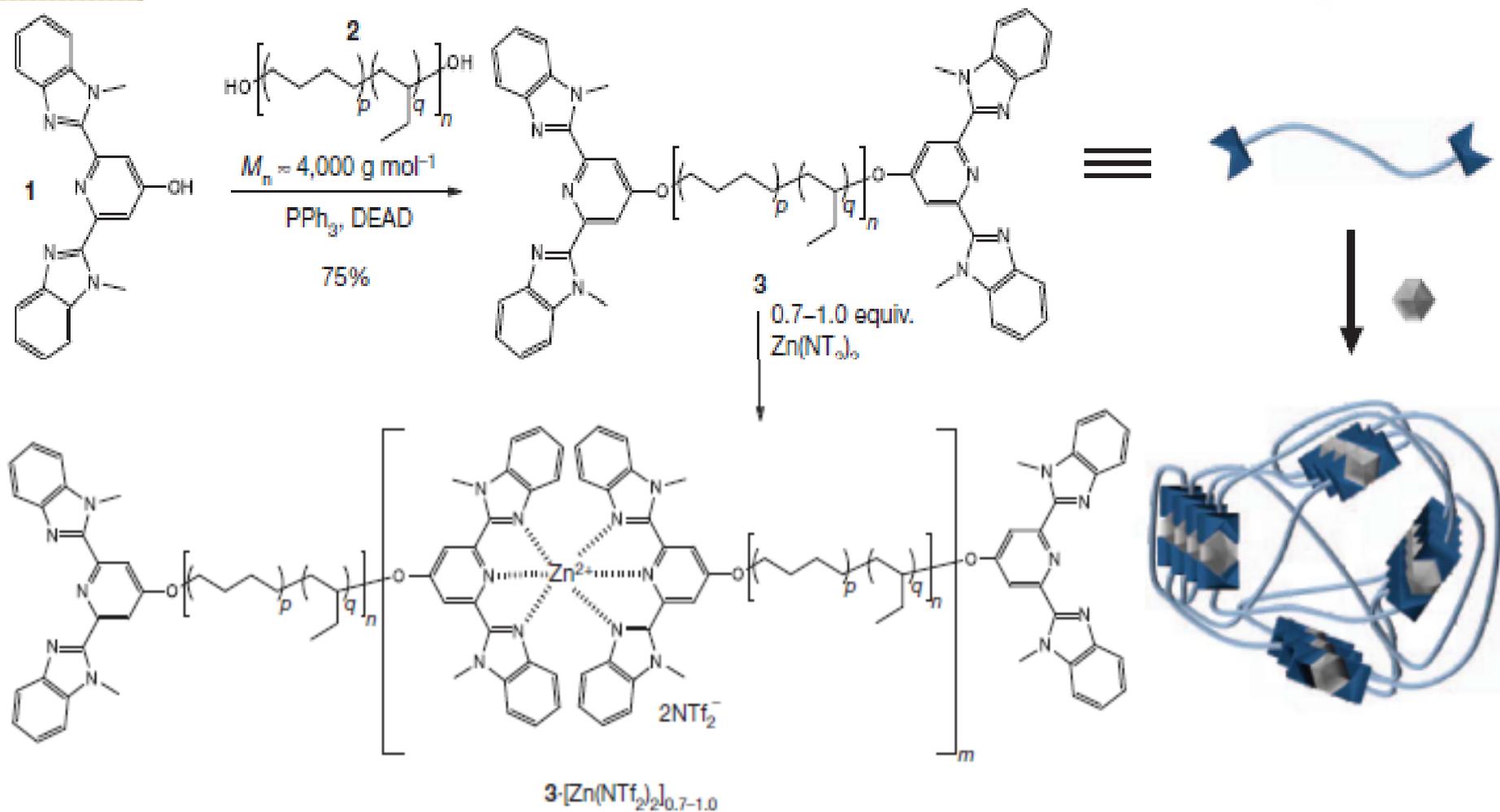
3- 3 . Noncovalent Bond Approach

3-3-1. Self-healing via metal-ligand interactions

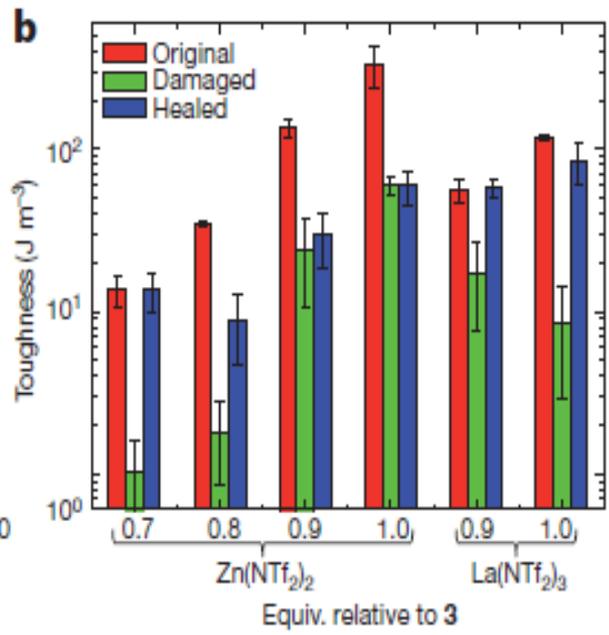
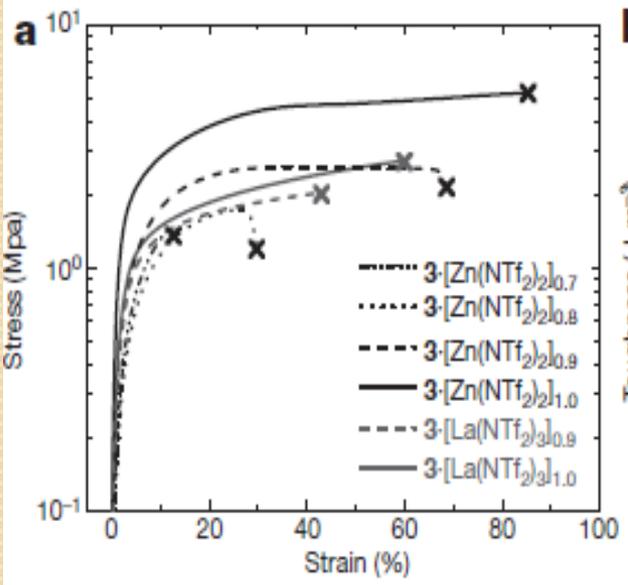
Working mechanism



Synthesis of this metal-ligands polymer system



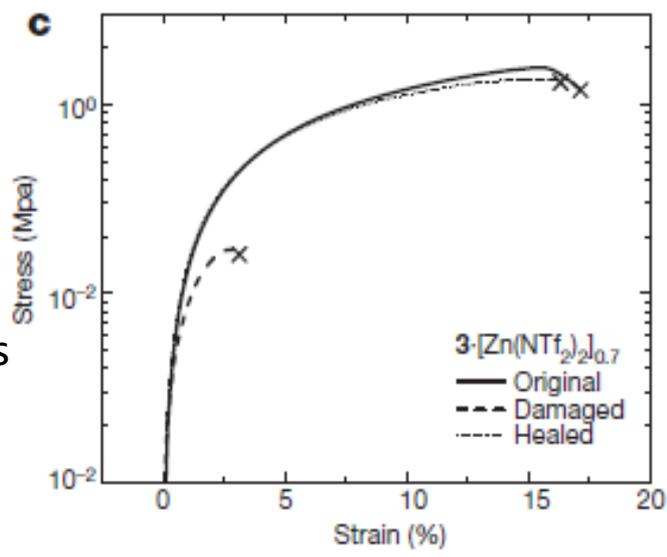
* $\text{La}(\text{NTf}_2)_3$ is also applicable to this system.



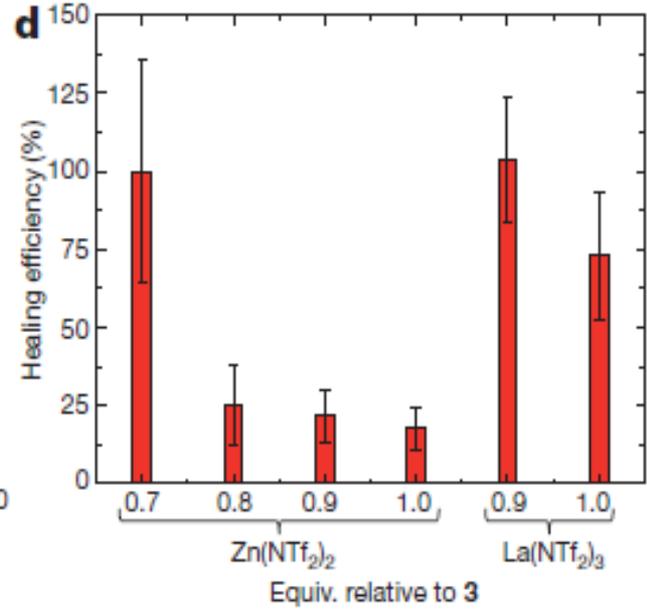
(a) Stress-strain curves of polymers of 3 and various amount of Zn(NTf₂)₂ or La(NTf₂)₃

(b) Toughness of polymers of 3 and various amount of Zn(NTf₂)₂ or La(NTf₂)₃

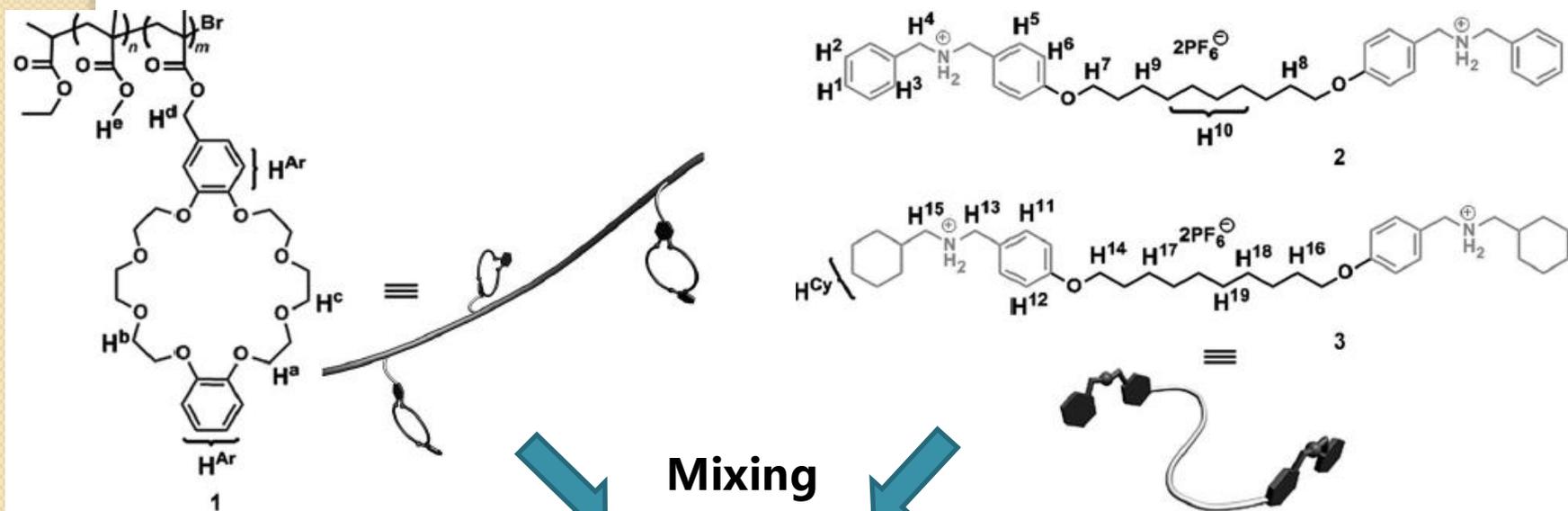
(c) Stress-strain curves of films of 3-[Zn(NTf₂)₂]_{0.7} of the original, damaged and healed examples.



(d) Healing efficiency of films of 3 and various amount of Zn(NTf₂)₂ or La(NTf₂)₃



3-3-2. Self-healing through crown ether based host-guest interaction

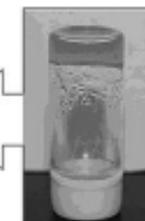
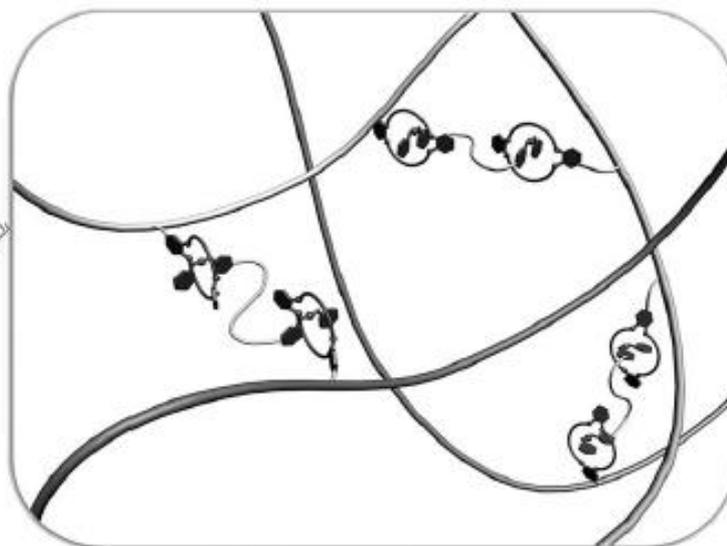


Mixing

Gel 4 can be obtained just by mixing 1 and 2 under r.t. in $\text{CHCl}_3/\text{MeCN}$ (1:1)



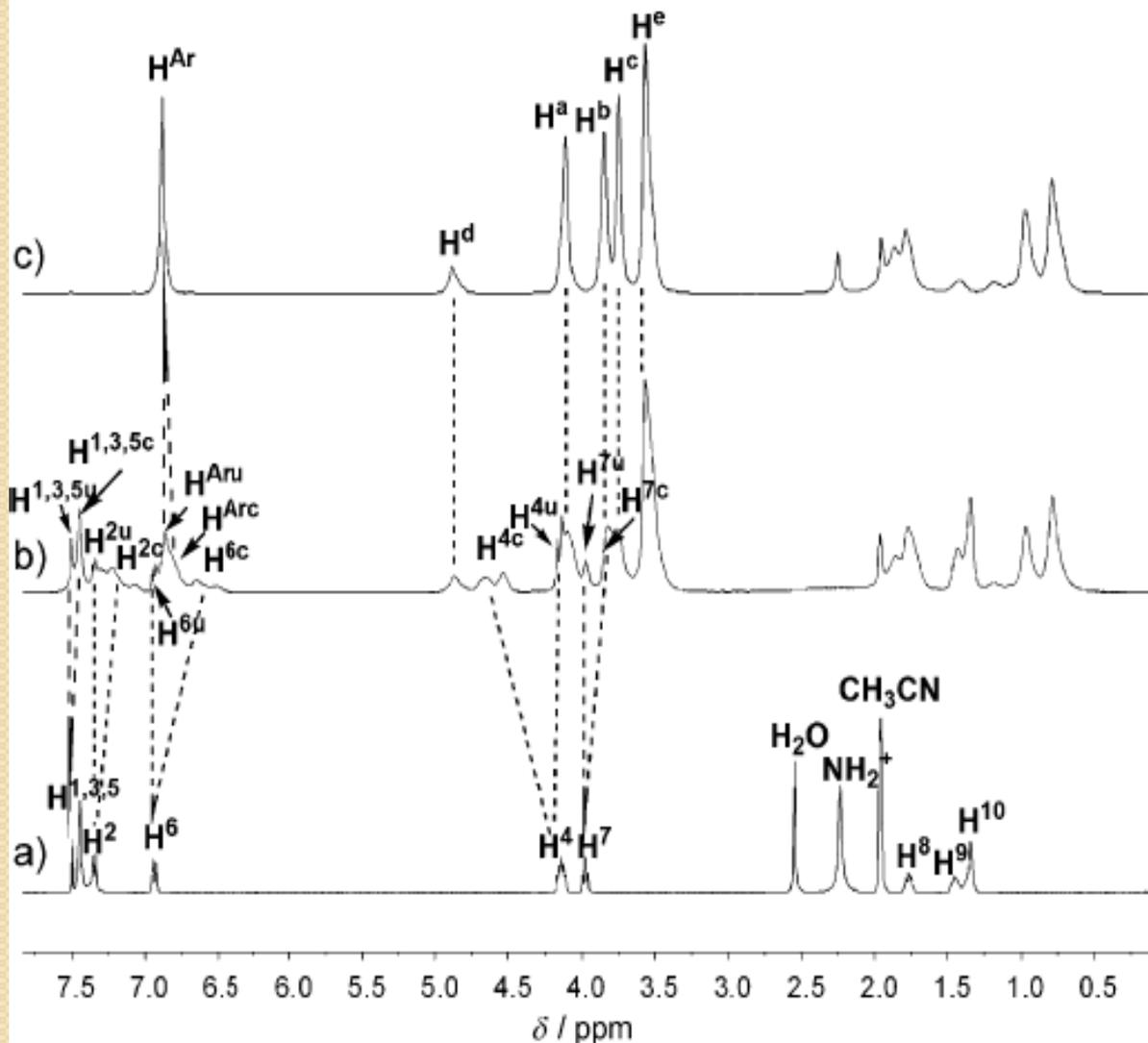
1 + 2
Gel 4



1 + 3
Gel 5

Gel 5 is formed from 1 and 3 by refluxing in $\text{CHCl}_3/\text{MeCN}$ (1:1) for 30d then stirring at r.t. for 45d.

Partial ^1H -NMR



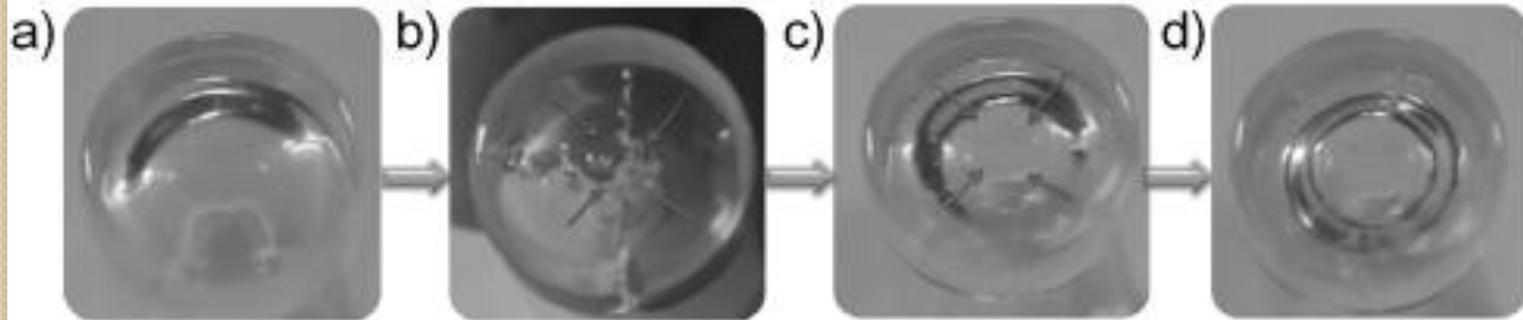
(c) Polymer 1

(b) Mixture of cross-linker 2 (3.6 mM) and polymer 1 (1.0 mM)

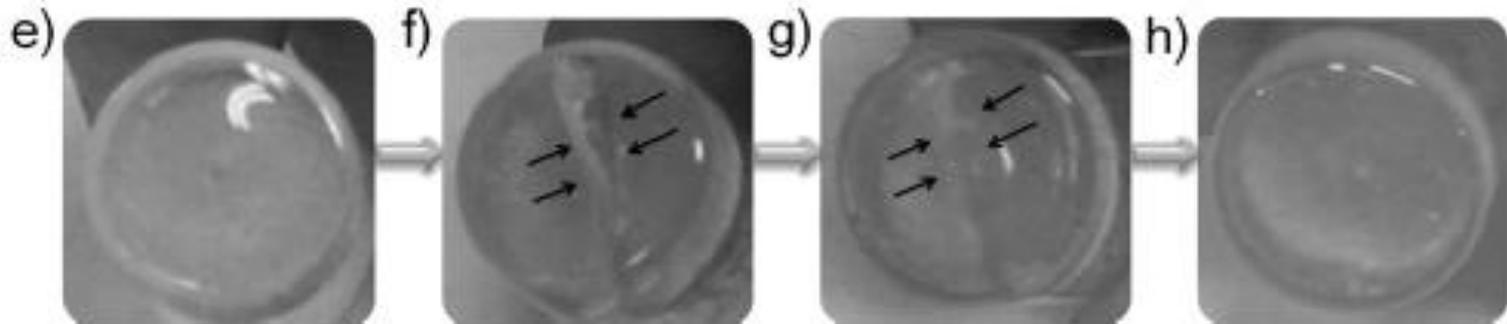
(a) Cross-linker 2

* "c" and "u" denote complexed and uncomplexed moieties respectively.

Healing experiment for Gel 4



Healing experiment for Gel 5

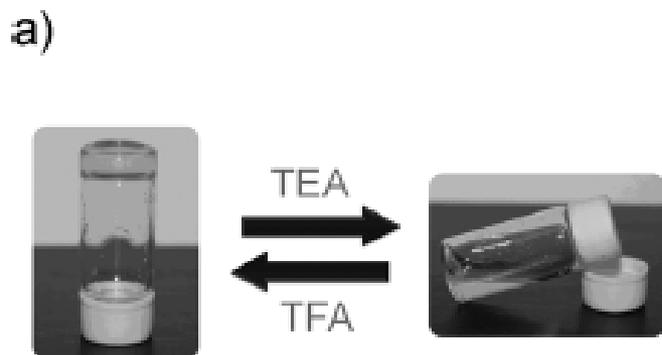


(a/e) Original Gel 4/5

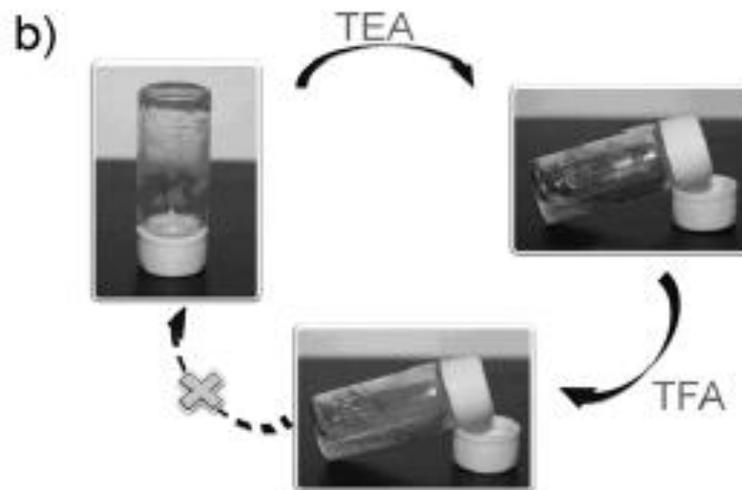
(b/f) Right after damage

(c/g) After free standing for 2 min

(d/h) After free standing for 4 min



Gel 4 can proceed reversible sol-gel transition by pH control

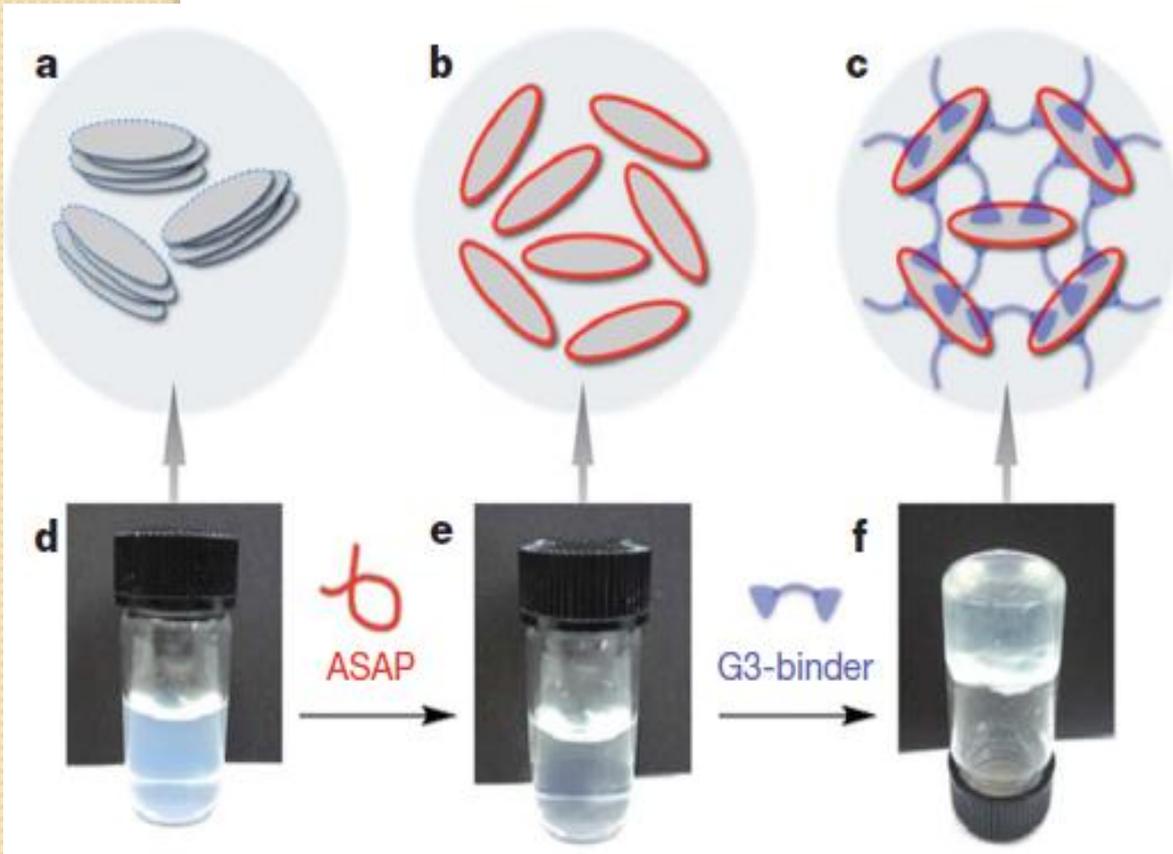


Gel 5 can be irreversibly degraded by TEA.

- ◆ Gel 4 and 5 both represents fast recovery with high healing efficiency (>95%).
- ◆ Both complexes are sensible to pH.
- ◆ Gel 4 and 5 adopts different healing mechanism:
 - *Gel 4's healing property is attributed to reversible interlocked crosslinking between crown ether and bisammonium salt.
 - *Gel 5's healing property is attributed to electrostatic and hydrogen-bonding interactions between 1 and 3 but not crosslinking between crown ether and bisammonium salt.

3-3-3. Self-healing through electrostatic interaction

Mechanism for hydrogel formation

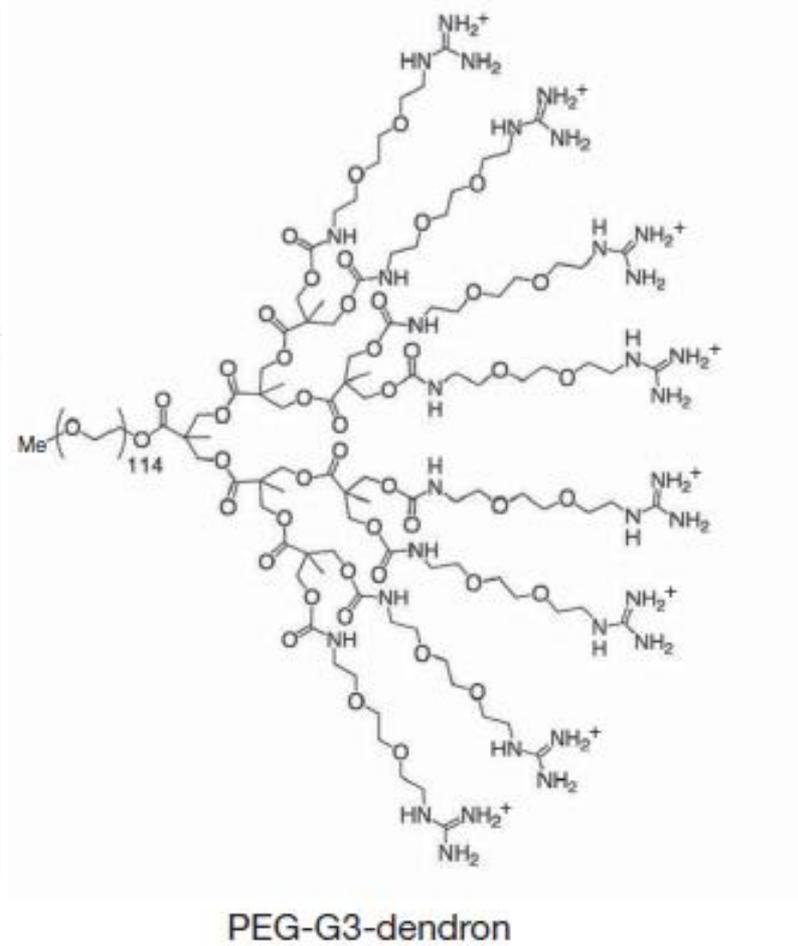
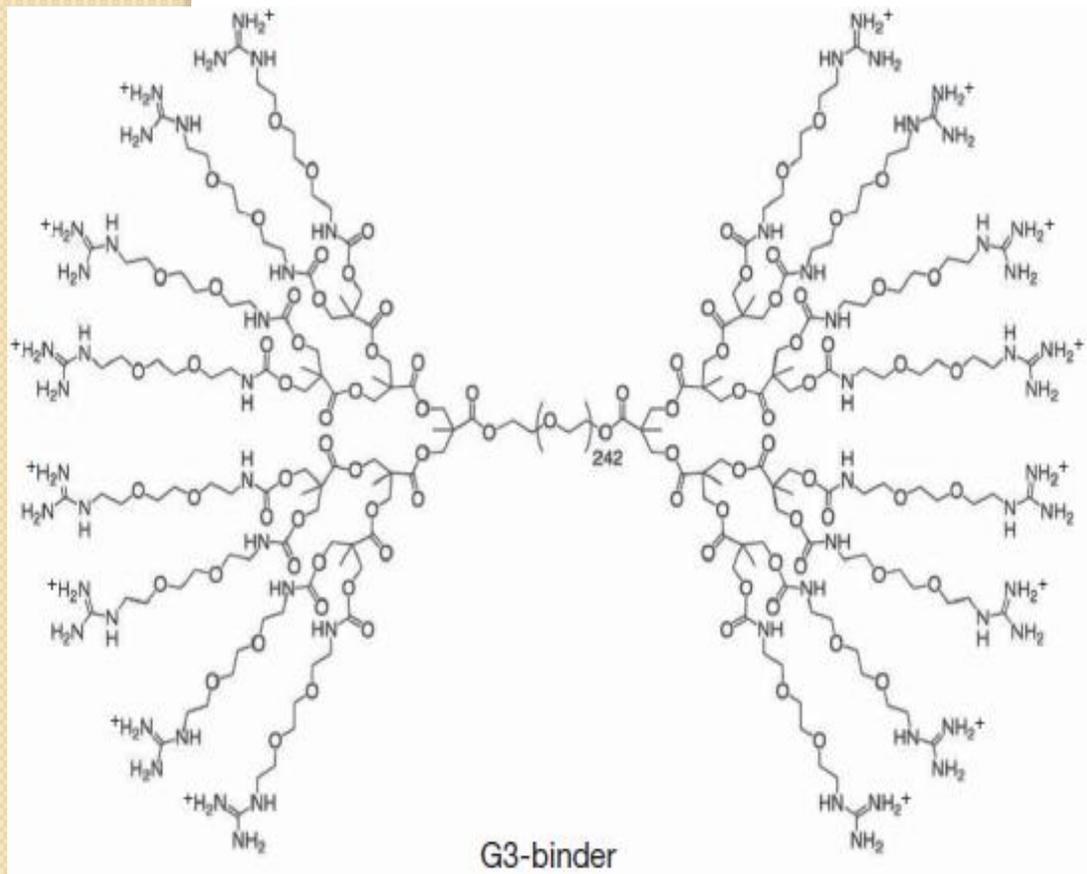


(a) Clay nanosheets (CNSs) entangled with each other at first

(b) CNSs are dispersed homogeneously by interaction of their positively charged edge parts with sodium polyacrylate (ASAP).

(c) Exfoliated CNSs are cross-linked to each other by a dendritic macromolecule (G3-binder) via electrostatic interaction.

Structure of G3-binder and its "half" analogue



Gn-binder compounds are reported to play as an efficient "molecular glue" via the interaction of its guanidinium groups with oxyanions on target compounds.

Healing experiment

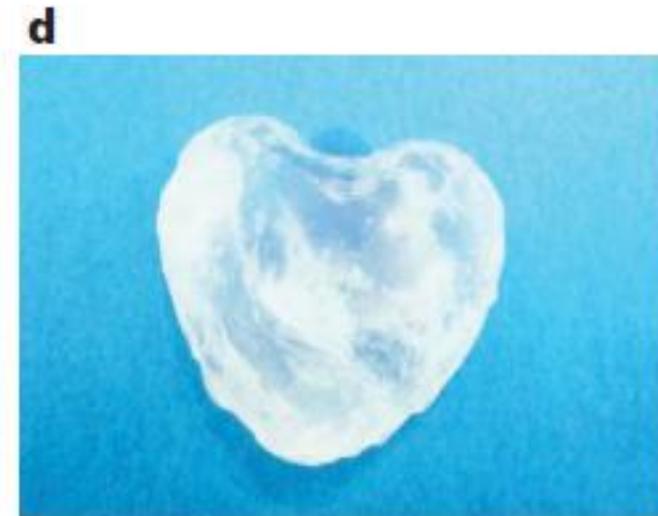


Hydrogels with or without 0.01% methylene blue were cut into 7 cuts. Then, place them one to another.

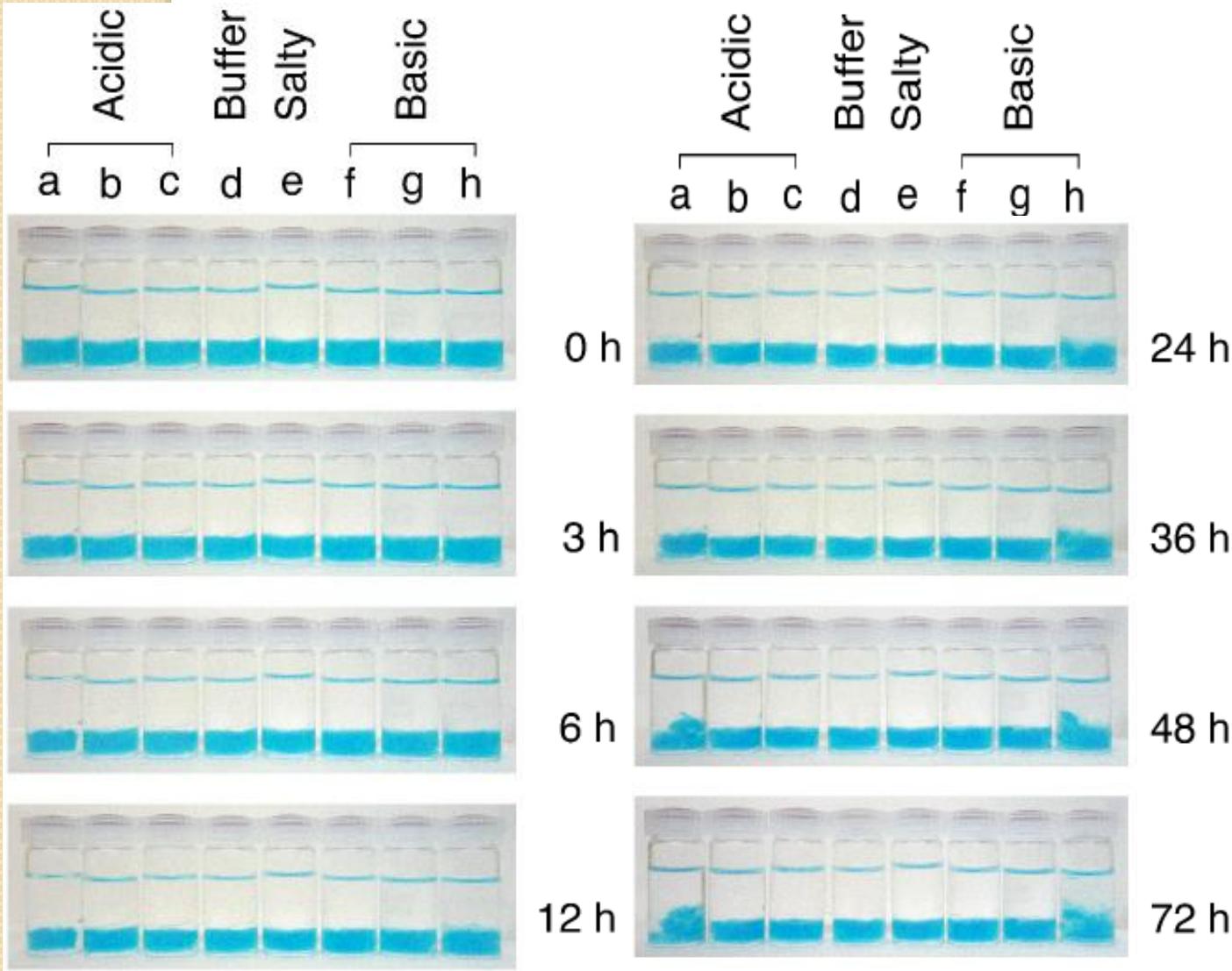
*(Hydrogel prepared by CNS 3.0%, G3-binder 0.21%, ASAP 0.09%, water 96.7%)

(c) Original heart-shaped sample of hydrogel

(d) Sample after being immersed for 6h three times in fresh THF at r.t.



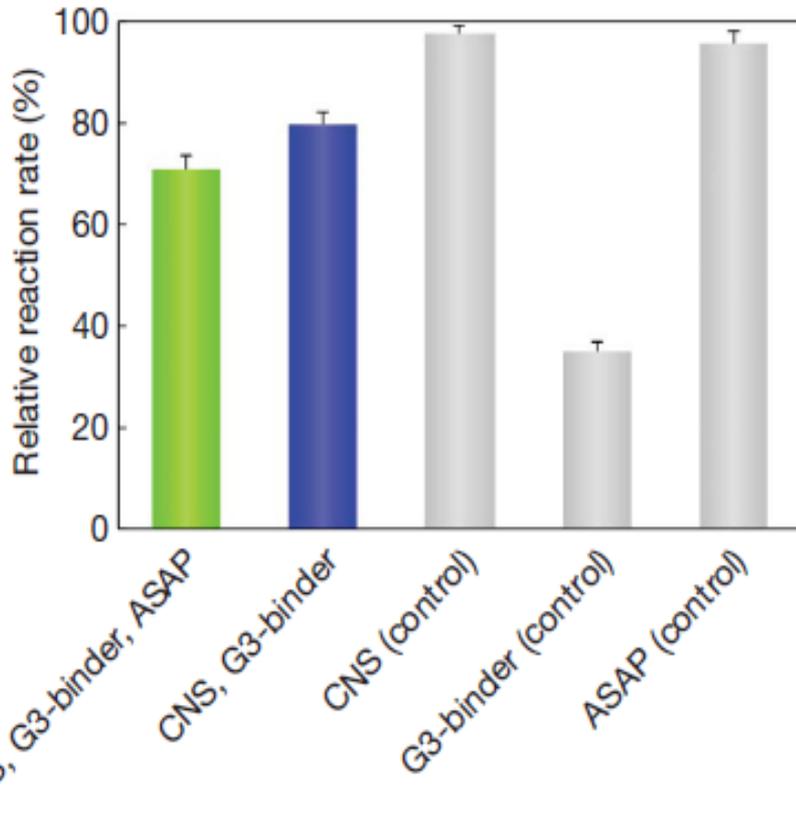
Stability test for pH, buffer and NaCl aq.



- Hydrogel samples are prepared by 2.0% CNS, 0.06% ASAP, 0.15% G3-binder and 0.01% methylene blue in water.

- Then 3 ml water with pH= 2.0[a], 4.0[b], 6.0[c], 8.0[f], 10.0[g], 12.0[h] or phosphate buffer(pH=7.4, 10 mM)[d], or 1M NaCl aq.[e]

Catalytic activities of myoglobin in hydrogels



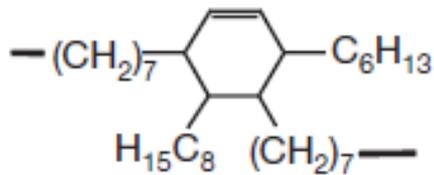
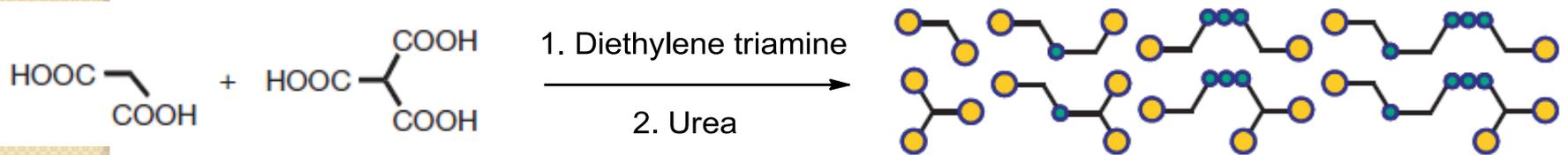
Hydrogels were prepared by mixing 2.0% CNS with 0.04% G3-binder in a 5.0mM aqueous solution of myoglobin with (green) or without (blue) 0.06% ASAP, and suspended in phosphate buffer containing o-phenylenediamine(10 mM) followed by H₂O₂ addition.

Characteristics of this system

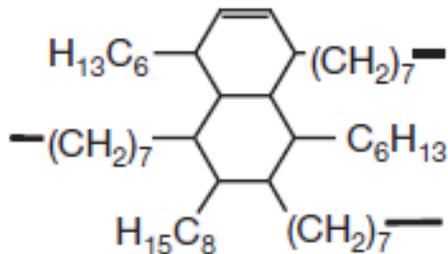
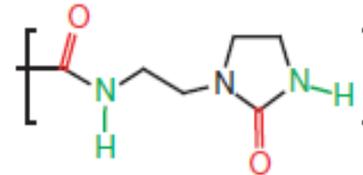
- ◆ Easy to prepare
- ◆ Stable and very environmentally friendly
- ◆ Excellent self-healing and shape retaining ability
- ◆ Mouldable into various shapes with satisfying mechanical strength.

3-3-4. Self-healing through hydrogen bond formation (1)

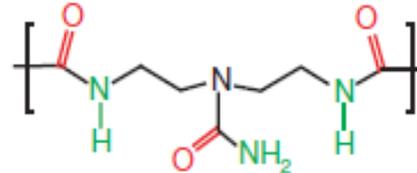
Key components & network forming scheme



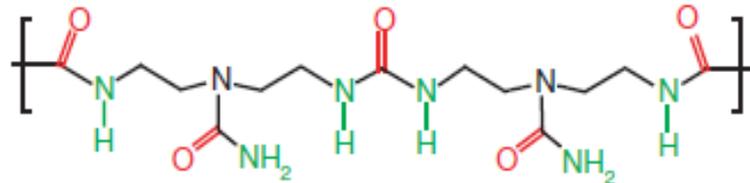
Amidoethyl imidazolidone



Di(amidoethyl) urea

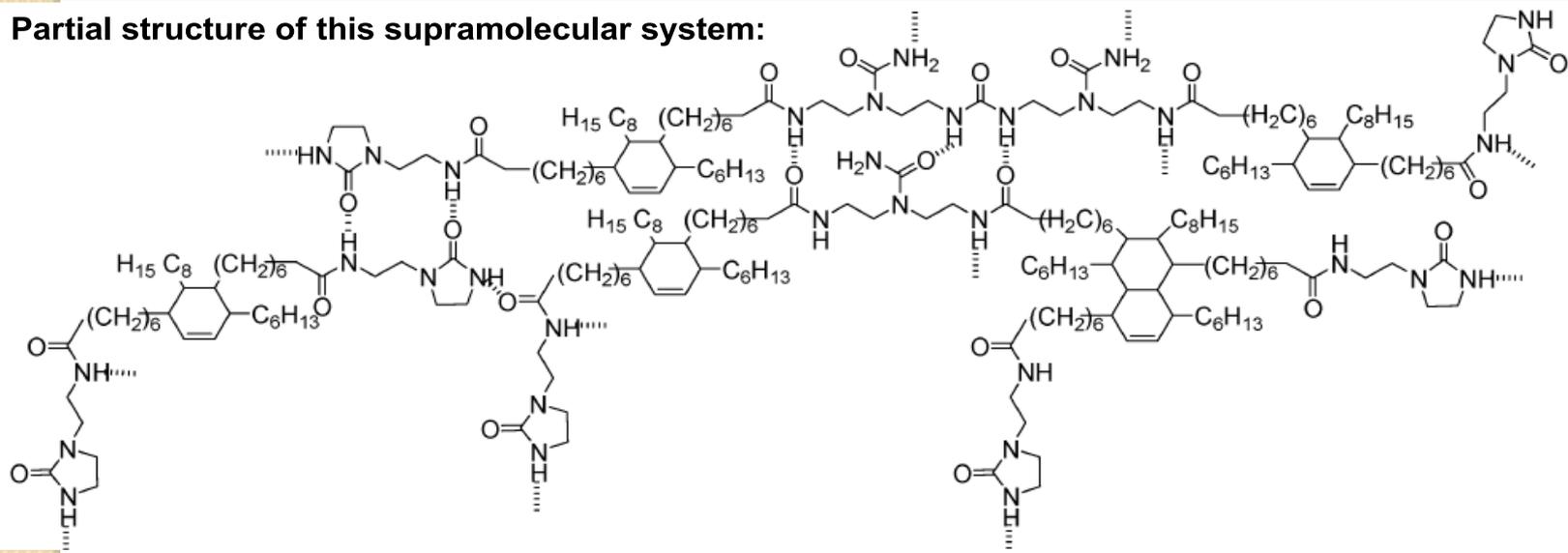


Diamido tetraethyl triurea



* H-bond acceptors are shown in red, donors in green.

Partial structure of this supramolecular system:

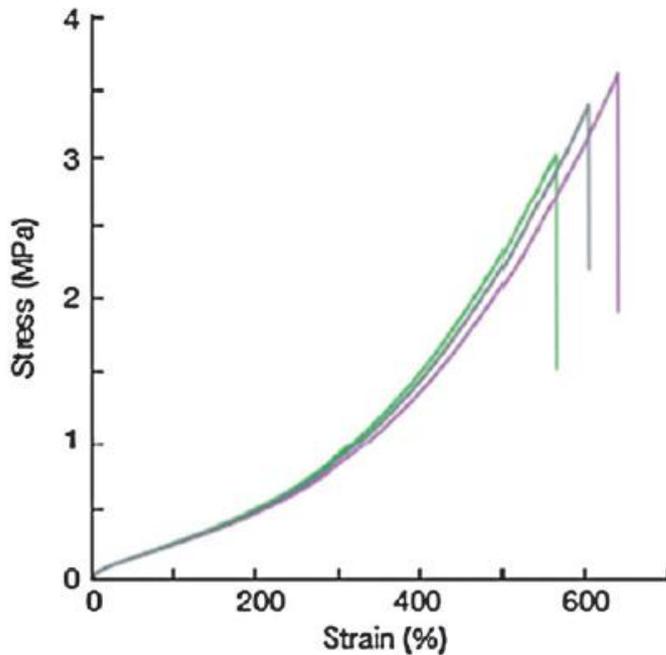


Healing experiment



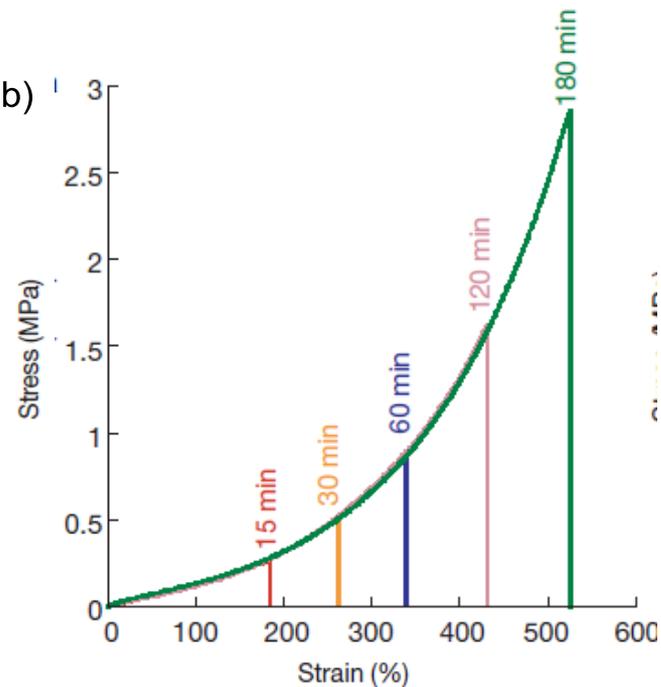
- Cut parts can heal by themselves by just be brought into contact at r.t.
- The higher the healing temperature is, the lower healing efficient is obtained.
- The longer time passes before putting the cutting ends together, the lower healing efficient is obtained.

(a)



(a) Stress-strain curves of this supramolecular rubber (Data of 3 samples)

(b)



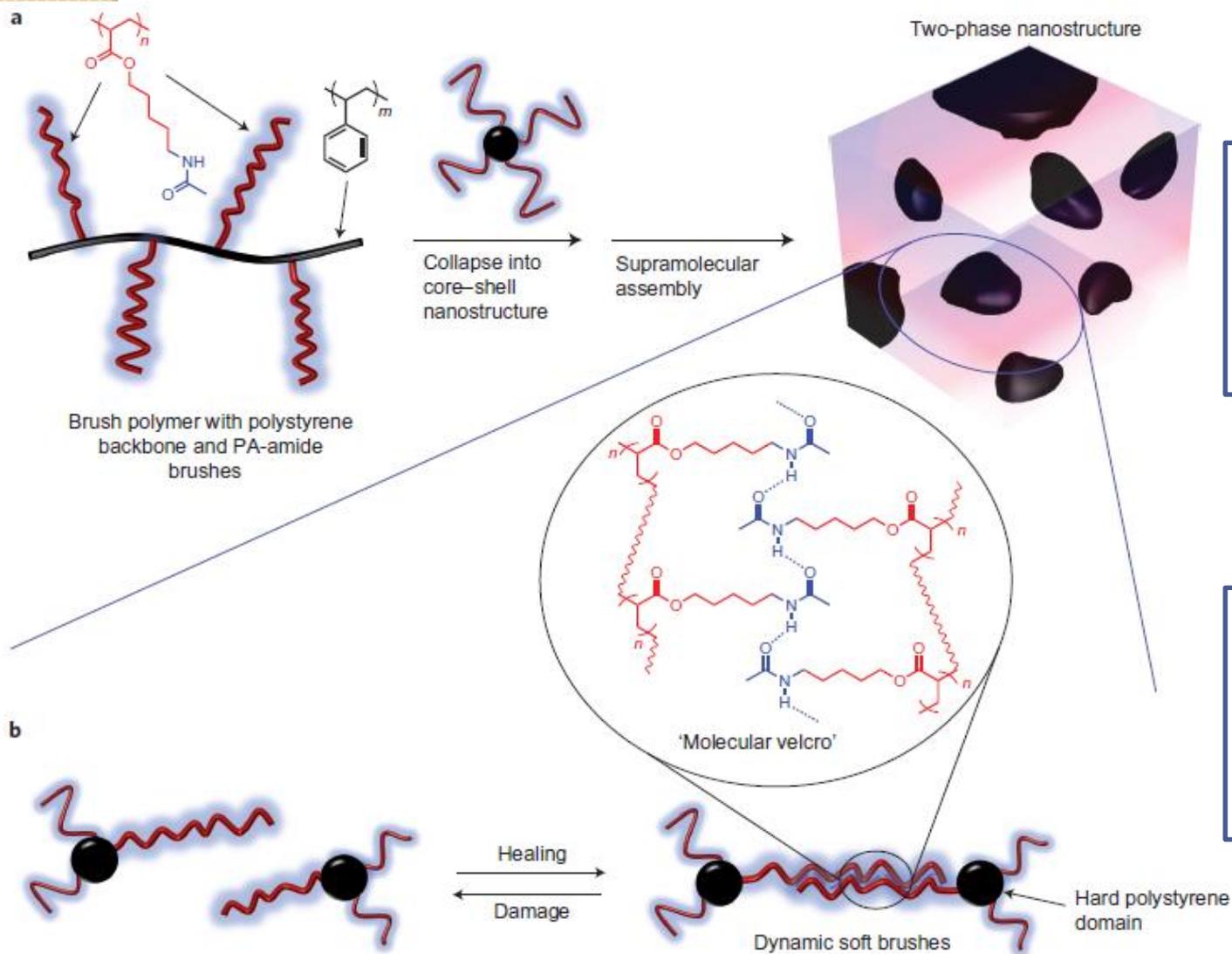
(b) Stress-strain curves of sample after different healing times at 20°C

Characteristics of this system

- Very simple healing conditions and free of external energy input
- Multi-time healing is possible with high healing efficiency
- Low cost of raw ingredients
- Easily being synthesized, re-used and recycled

3-3-4. Self-healing through hydrogen bond formation (2)

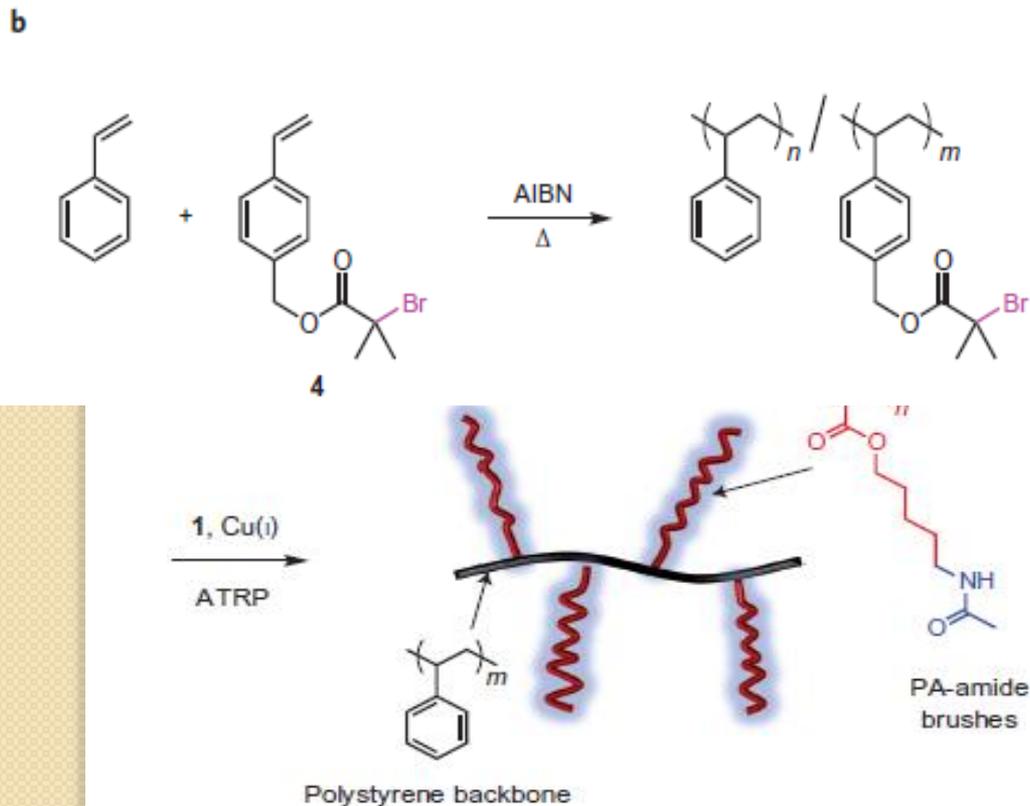
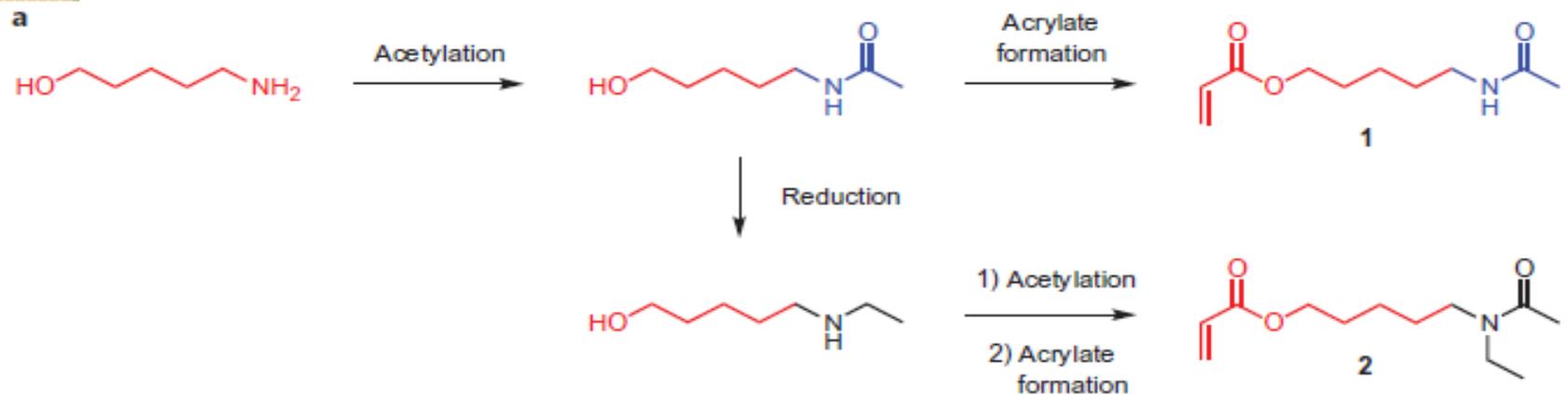
Working scheme



- Unique hard-soft multiphase system merging properties of stiff and tough polymers with dynamic assemblies.

- Dynamic healing motifs are designed as the soft phase in a hydrogen-bonding brush polymer (HBP).

Synthesis of HBP material system



(1) Styrene is first copolymerized with an ATRP co-monomer **4** via free-radical polymerization.

(2) Following ATRP polymerization with monomer **1** is carried out to form brushes.

* ATRP stands for "atom transfer radical polymerization".

Ref. : K. Matyjaszewski *et al.*
Science, **1996**, *272*, 866

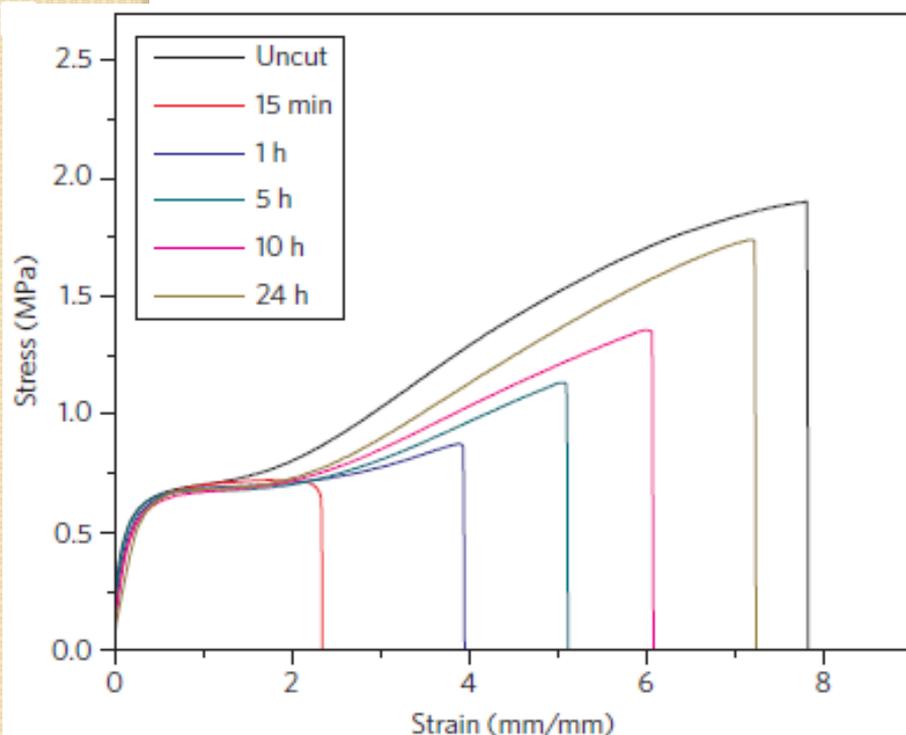
Molecular character

Mechanical properties

Healing efficiency (%)

Sample	Molecular character		Mechanical properties			Healing efficiency (%)	
	Polystyrene backbone repeat units (Br/chain)	PA-amide brush repeat units	Yield strength [†] (MPa)	Strain-at-break* (%)	Strength-at-break* (MPa)	1 h	24 h
HBP-1	114 (11)	186	0.26±0.02	1570±40	0.9±0.05	42±2	79±2
HBP-2	114 (11)	84	0.48±0.02	780±15	1.92±0.18	51±3	90±4
HBP-3	100 (5)	194	0.89±0.04	310±6	3.77±0.32	40±1	75±2
Control-1	-	193	-	-	-	-	-
Control-2	114 (11)	220	-	-	-	-	-

Healing experiment



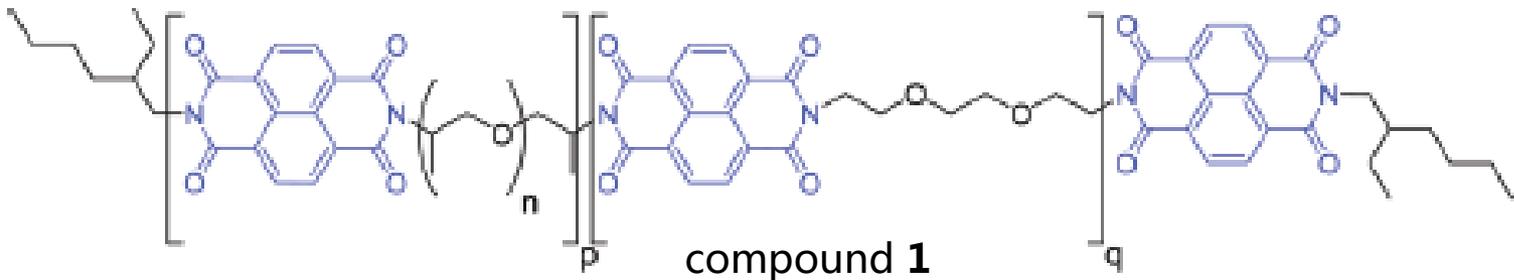
*Sample cut into completely separate pieces and then brought together to heal at room temperature.

Characteristics of this system

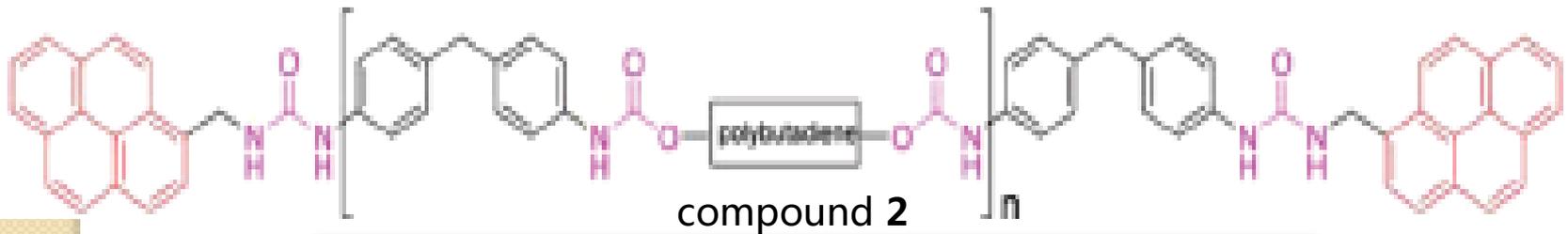
- Very simple healing conditions and free of external energy input
- Multi-time healing is possible with high healing efficiency.
- Excellent mechanical properties
- Easily being synthesized, re-used and recycled

3-3-5. Self-healing through pi-pi stacking and hydrogen-bonding interactions

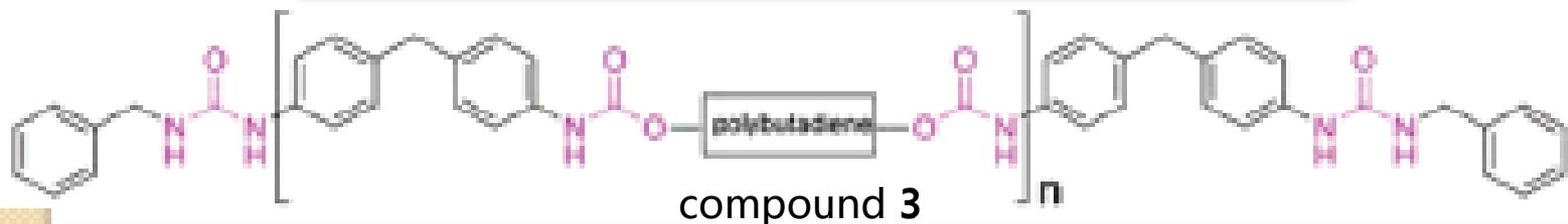
Key components in this system



polyimide with a p-electron-deficient bis(diimide) motif

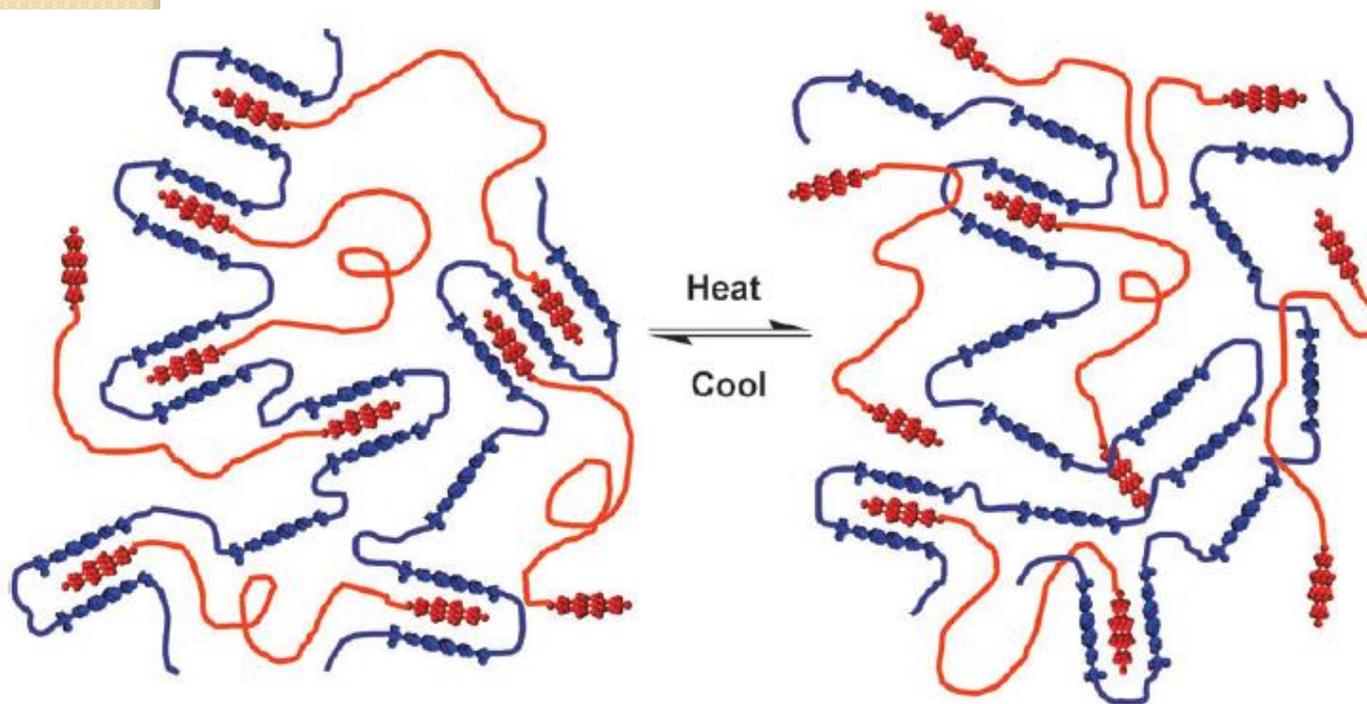
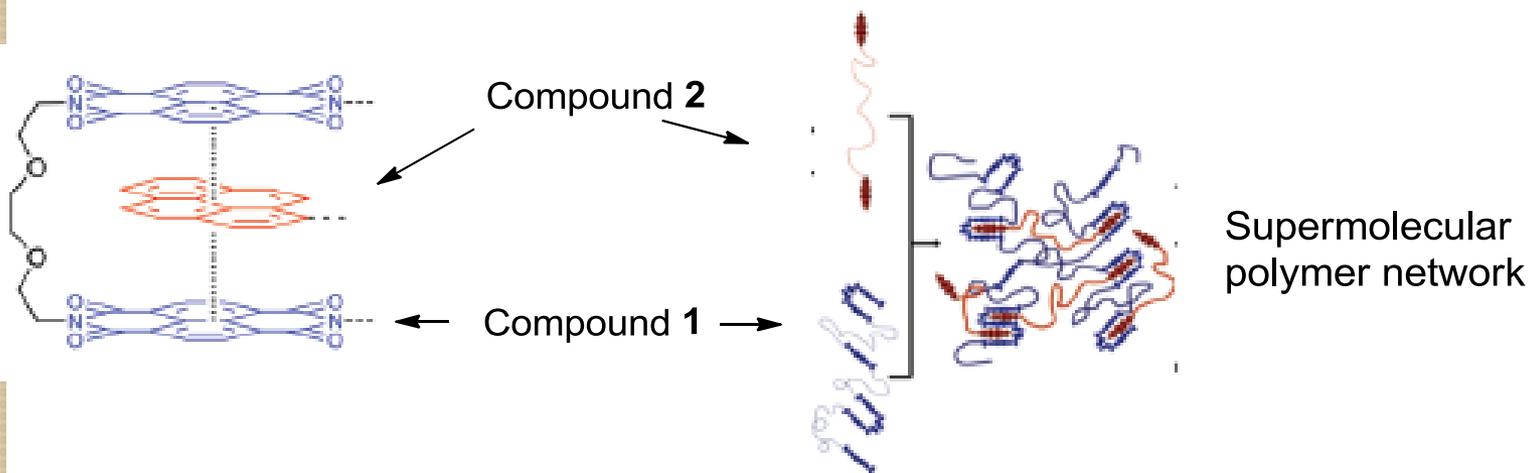


polyurethane with p-electron-rich pyrene moiety

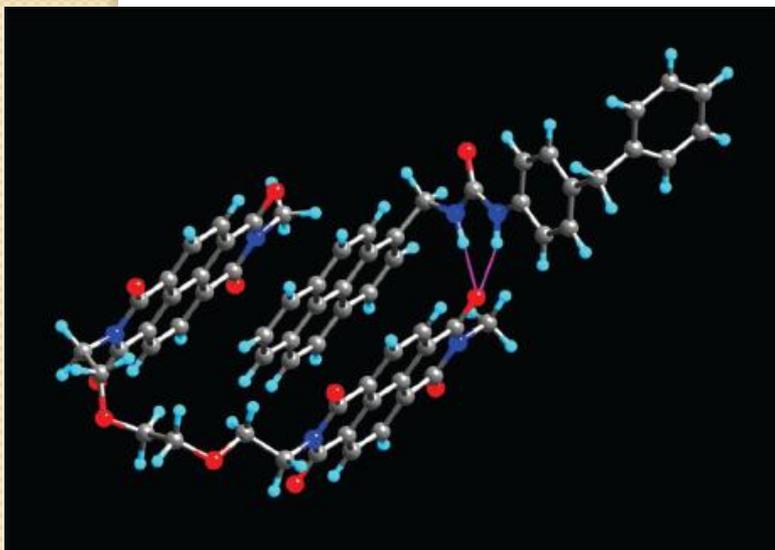


polyurethane with terminal benzyl group instead of pyrenyl moiety in compound 2, used in control experiment

Working scheme



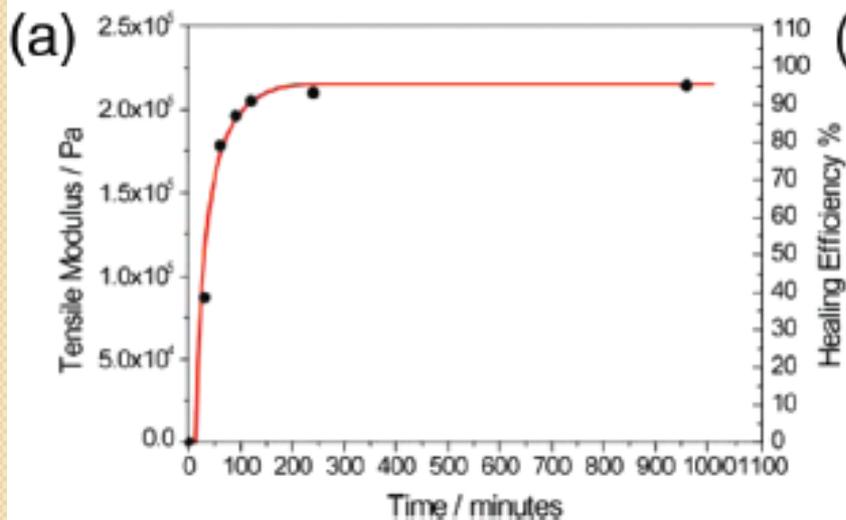
p-p stacking and H-bonds get disengaged at heating, after random diffusion, new network reforms when cooling.



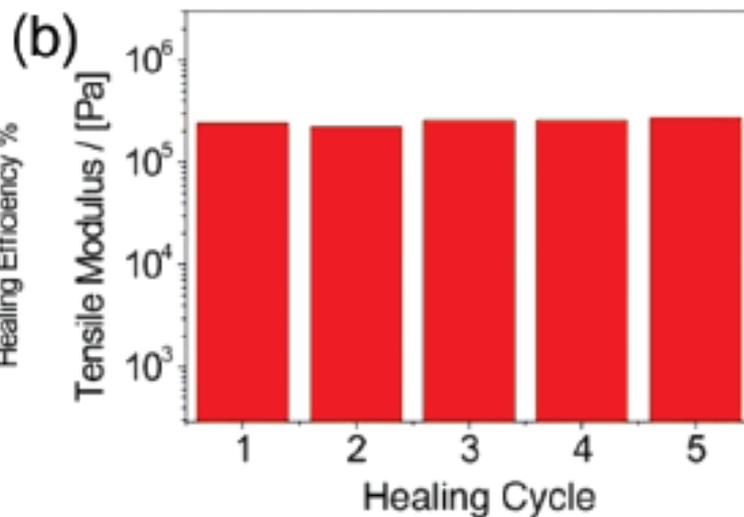
Minimized computational model of the interaction between diimide moieties and pyrenyl group in compound 1 and 2.

- Electronically complementary triple p-stack was formed.
- A pair of strong, convergent hydrogen bonds from the urea unit to a diimide group were formed.

Healing experiment (1)



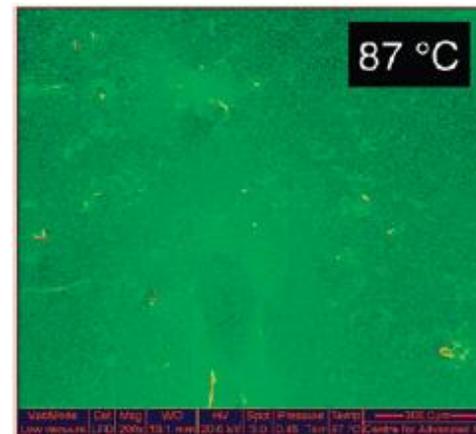
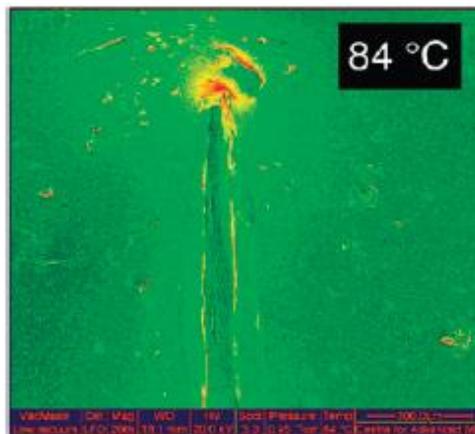
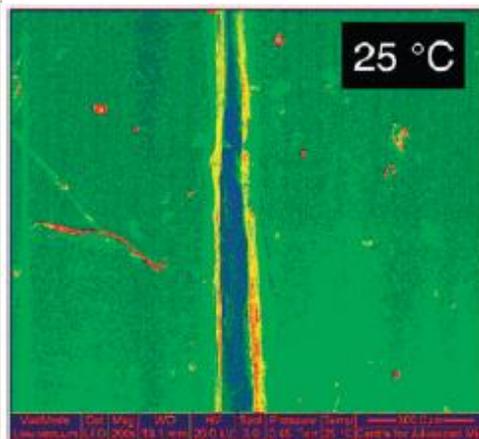
(a) Healing efficiency of network [1+2] as function of time (Healing temp is 100C)



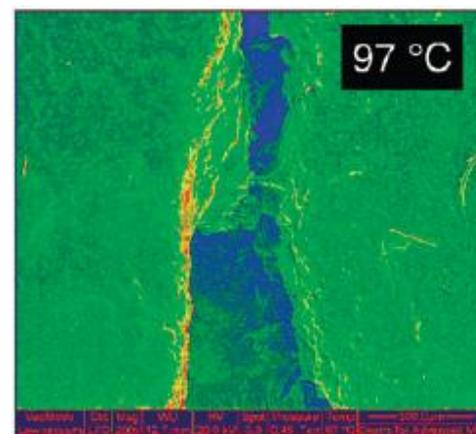
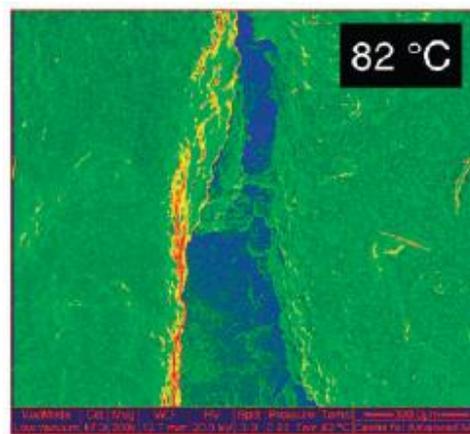
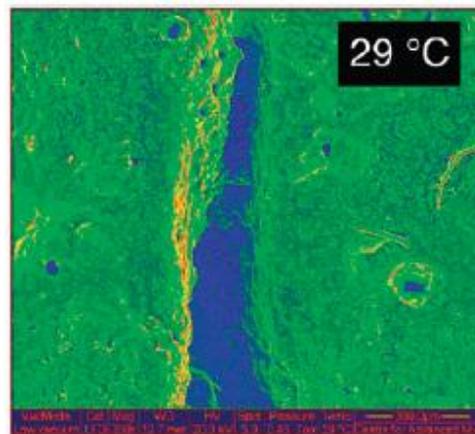
(b) Recovery of the tensile modulus for network [1+2] sample over break-heal cycles.

Healing experiment (2)

Network [1+2]



Control sample [1+3]



* False-color ESEM images at different healing temperature.

S.J. Rowan *et al.* *JACS*, **2010**, *132*, 12051-58

Summary and perspective

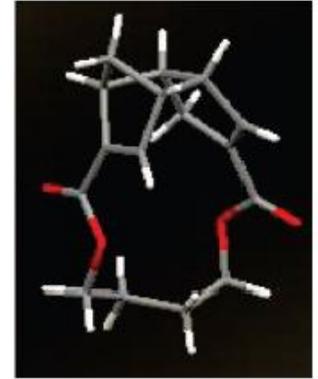
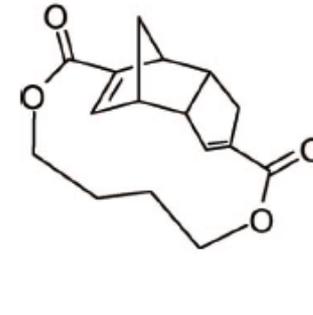
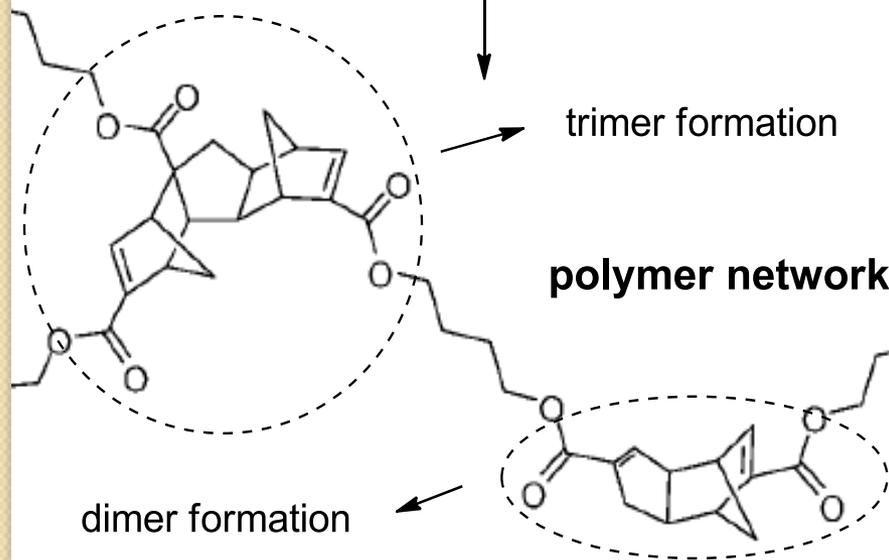
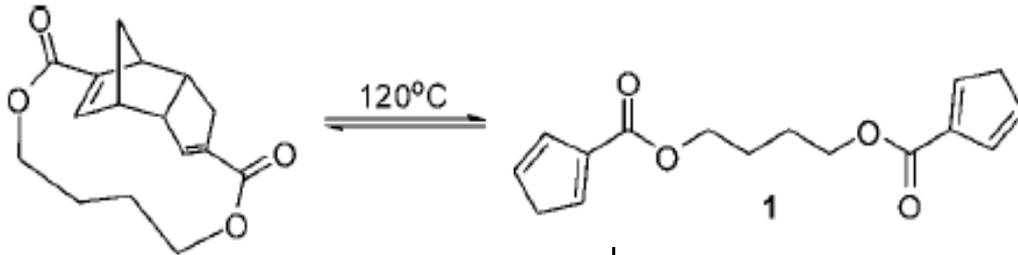
	Pros	Cons
Capsule-based	free of external stimuli, various combination	single time healing, limitation in encapsulation method
Microvascular	free of external stimuli, various combination, multi-time healing	Difficulty in network design
Reversible covalent bonding	multi-time healing, good mechanical strength	generally requiring external stimuli, lack in varieties on design
Chain reentanglement	good mechanical strength	single time healing, lack in varieties on design
Noncovalent bonding	multi-time healing, various combination, generally free of external stimuli	generally bad mechanical strength

- New materials that employ cross category design are expected.
- Materials towards more biomimetic manner may come into trend.



3-1-2. Single-Component Thermally Remendable Polymer Network

Working scheme



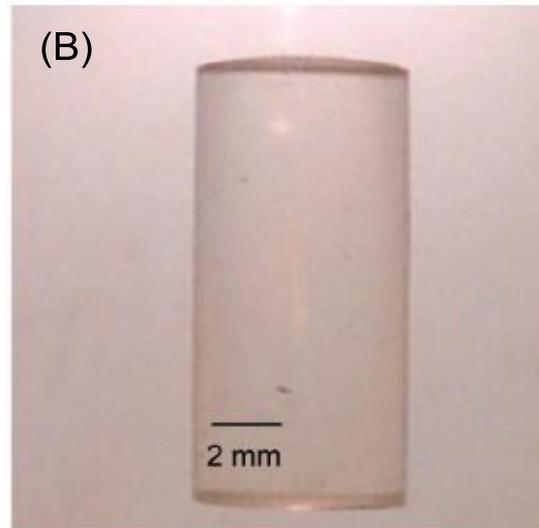
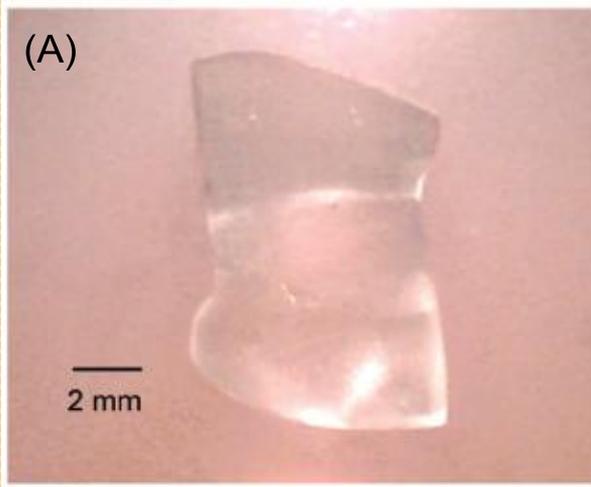
Monomer 400 and its X-ray crystal structure

- Retro-DA reactions first take place when heating to 120C to generate di-cyclopentadiene monomer.
- Then heating up to 150C for 10h followed by slow cooling to r.t. to get polymer network.
- Not only dimer but also trimer formed which enabled cross-linking formation.

Characteristics of this system:

- ◆ Healing could be achieved by just heating at 120C.
- ◆ Multi-time healing is possible but only moderate healing efficiency.
- ◆ Especially efficient in shape recovery
- ◆ Single component but with high cross-links.

	sample		fracture strength [N]	recovered strength [%]
polymer 400	1	virgin sample	201	
		after 1st healing	103	51.2
		after 2nd healing	48	46.6
	2	virgin sample	205	
		after 1st healing	100	48.8
		after 2nd healing	40	40
3	virgin sample	750		
	after 1st healing	150	20	
	after 3rd healing	17	42.5	
4	virgin sample	390		
	after 1st healing	232	59.5	
	after 2nd healing	135	58.2	



(A) Polymer specimen right after compression testing

(B) After healing, identical shape to the pretest state