西 安 交 通 大 学

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Soft Nanomaterials of POSS-based Copolymer for Arts Conservation

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1. Background





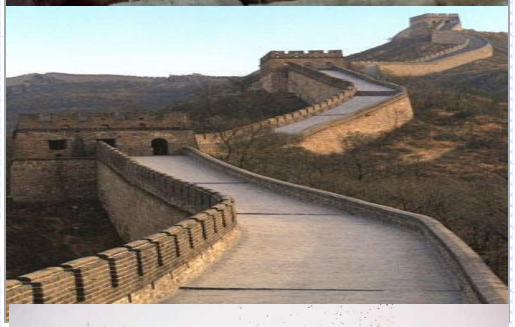




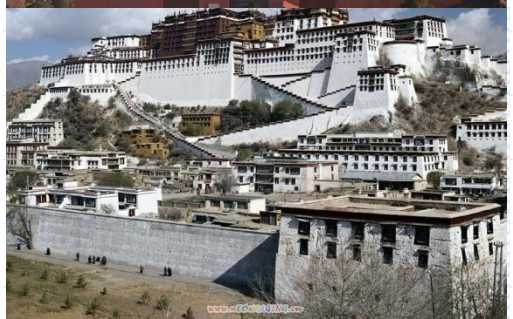




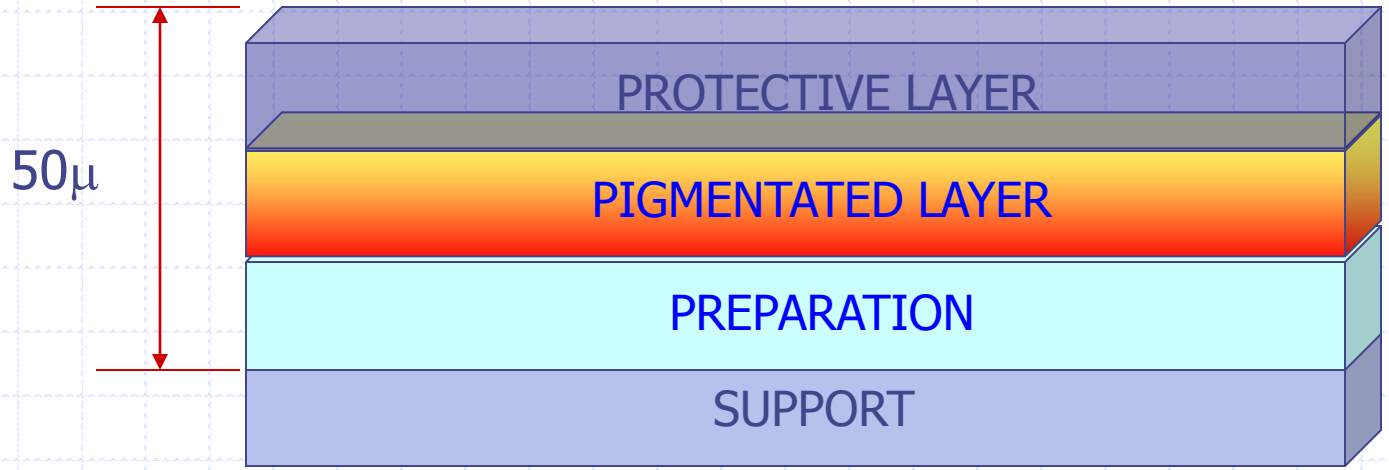








PAINT STRATIGRAPHY





*** support: wood, stone, clay, fiber, brick……**

*** pigments: nature minerals and dye**

**** binding medium: nature organic materials or polymers***

What happened with time ?

The main problem of these precious heritages?













Lost the bindings and colors because of the water and salt.

Silicate Cultural heritage is a special patient:

- ✓**It holds values (cultural, historical, esthetical, material,……)**
- ✓**It ages in an *irreversible* way with time**
- ✓**It is a *passive* patient (doesn't speak and doesn't complain!!)**

The patient doesn't go spontaneously to the doctor but need to be protected.

Who are the doctors???













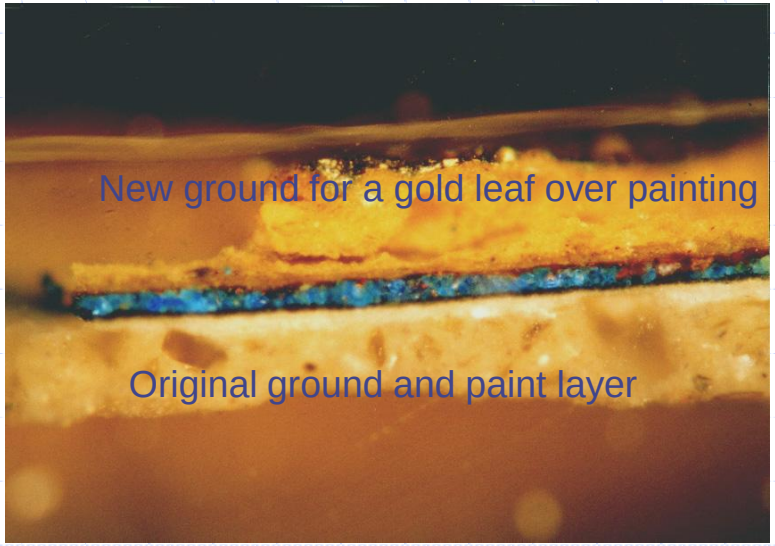
Conservation scientist

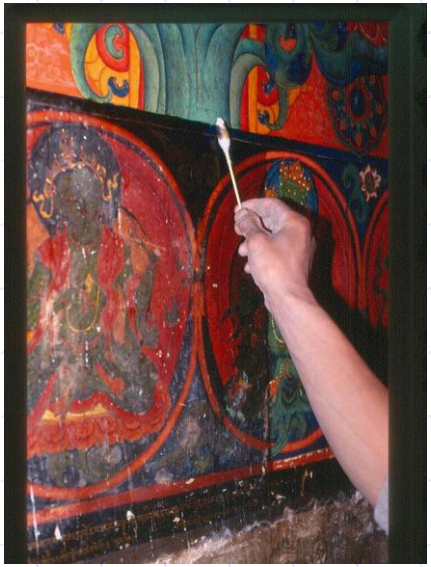
Conservator-restorer

Art historian/ archaeologist

Is it possible to perform surgery (*restore)* on a patient without knowing his case and history (*anamnesis*)?

(i.e.: materials over paintings, techniques, past restoration, the properties of protective materials)







The problems need to be solved

* Understand the real nature of original materials

* Develop useful and reliable materials for the protection

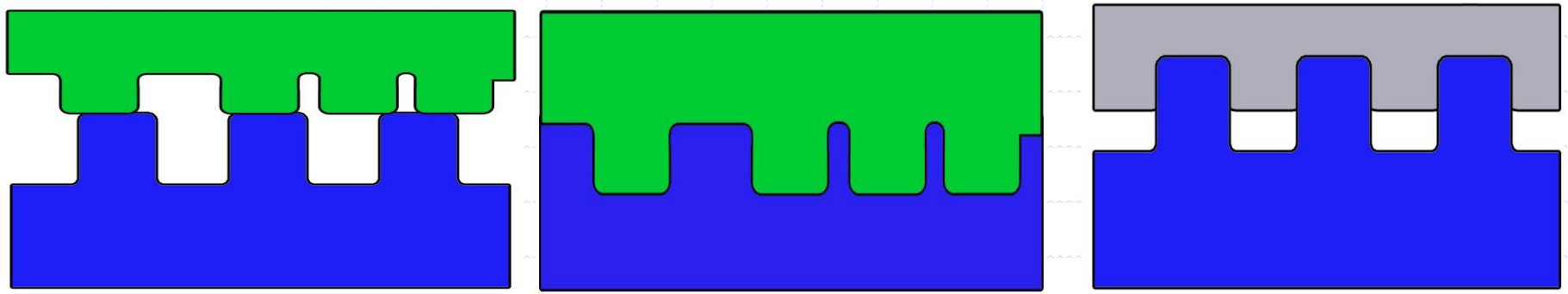
* Establish protective methods

The functional materials should be the idea candidate

Requirements of materials for conservation of artworks

The basic requirement for the materials???

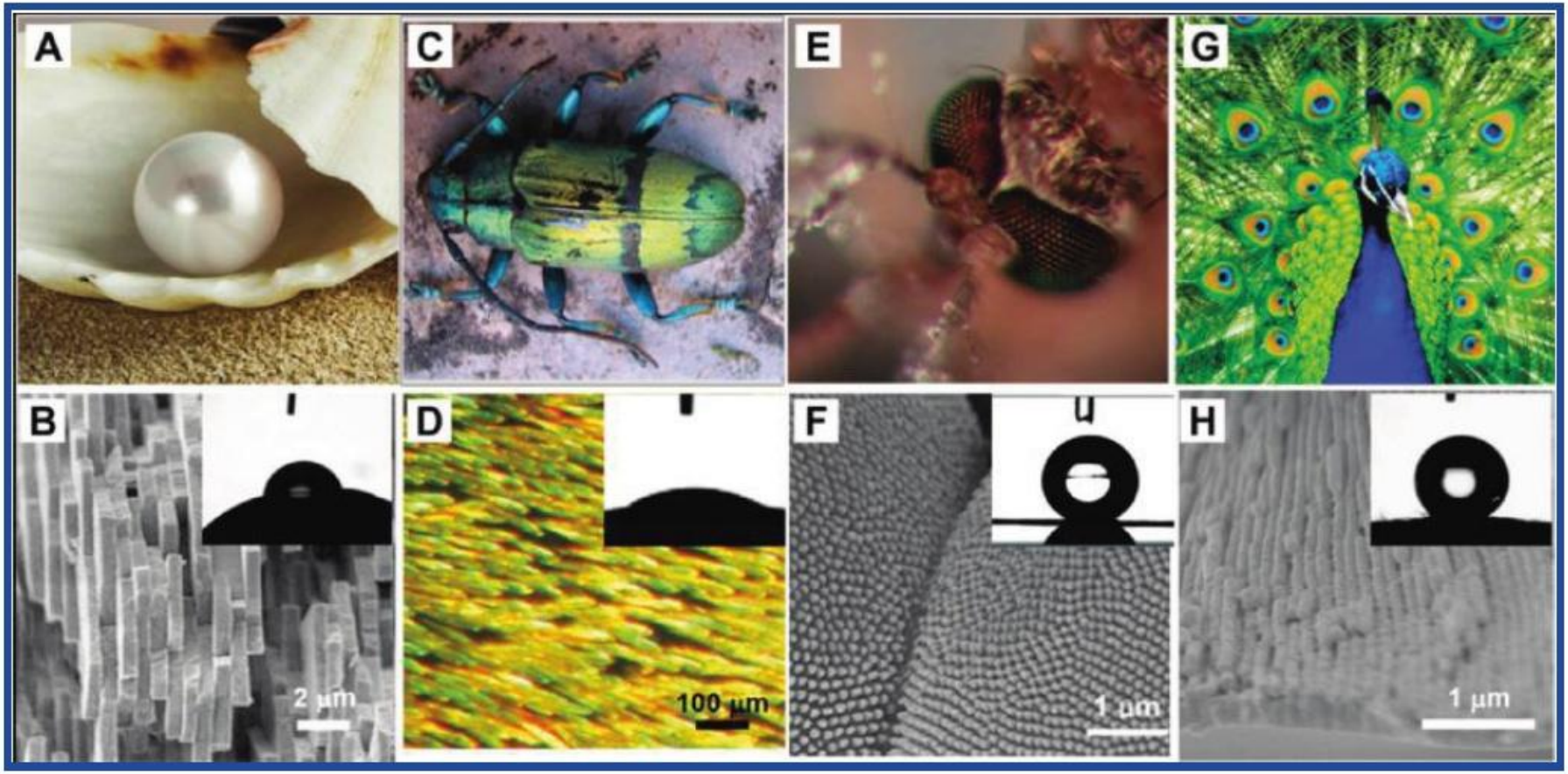
- ✓ Security and harmless to relics
- ✓ Suitable respiratory function
- ✓ Conformable chemical and physical properties with substrate
- ✓ Influence on the follow-up retreatment



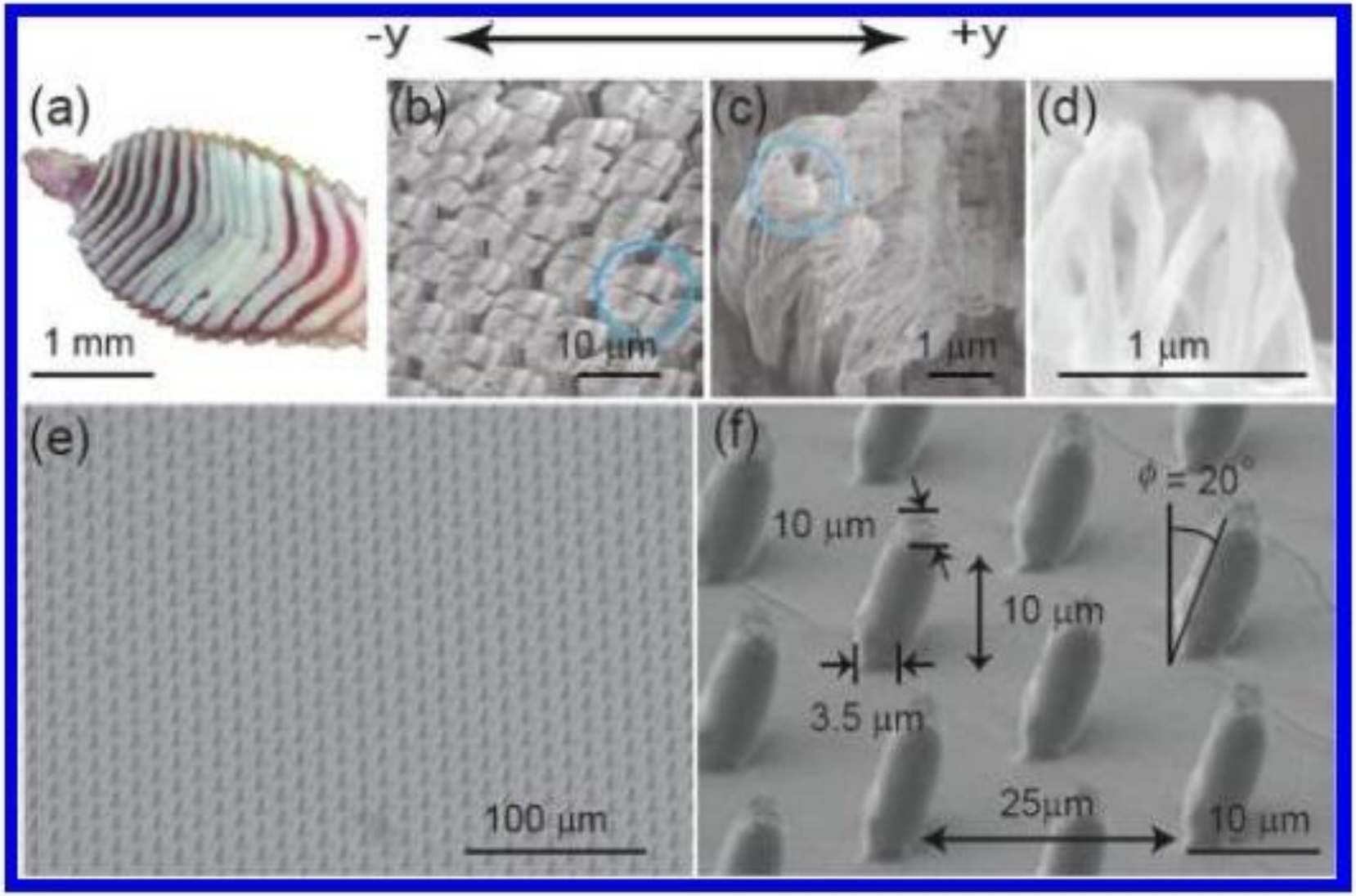
Challenge

- The design and realization of function materials

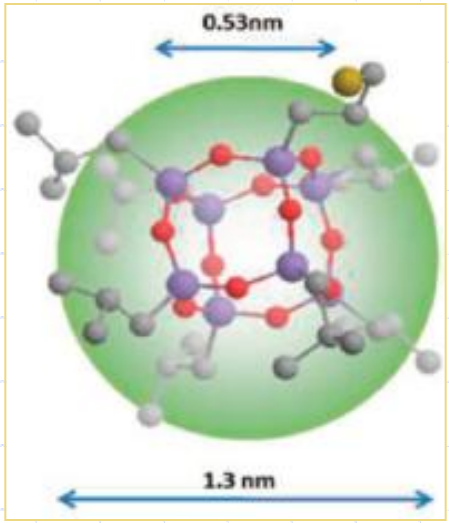
Periodic structures with special wettability in nature



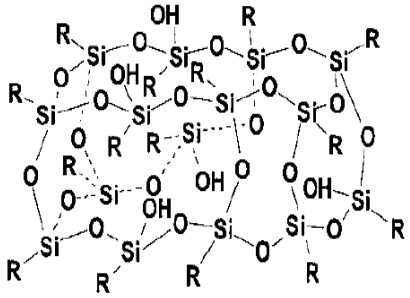
(A, B) hydrophilic pearl (water CA=45°);
(C, D) hydrophilic longhorn beetles Tmesisternus isabellae (water CA =25°);
(E, F) superhydrophobic mosquito eye (water CA = 149.8°);
(G, H) superhydrophobic peacock (water CA =150°).


-y
+y
(a)
1 mm
(b)
10 μm
(c)
1 μm
(d)
1 μm
(e)
100 μm
(f)
10 μm
10 μm
3.5 μm
φ = 20°
25μm
10 μm

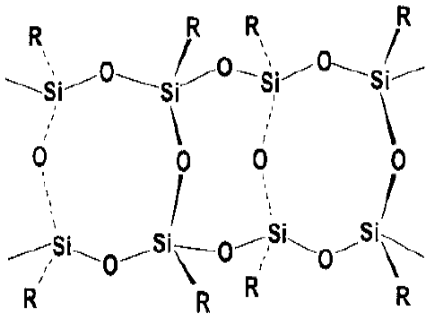
Polyhedral Oligomeric Silsesquioxanes (POSS)



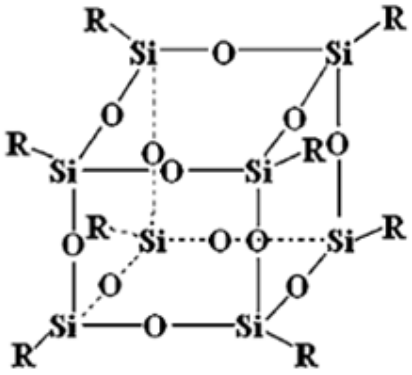
1-3nm molecular dimension



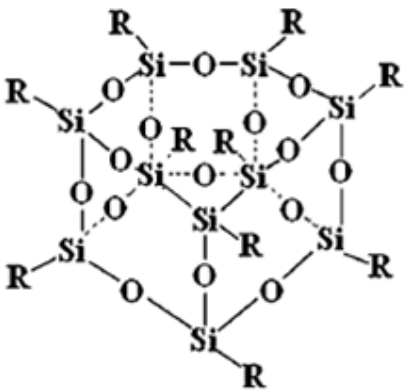
(a)
Random structure



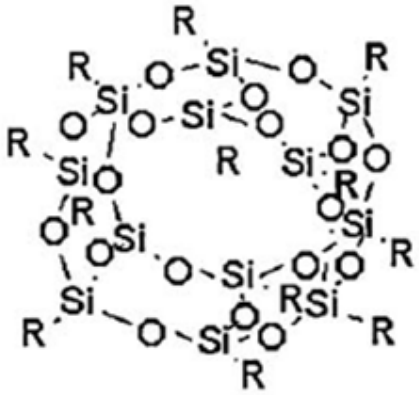
(b)
Ladder structure



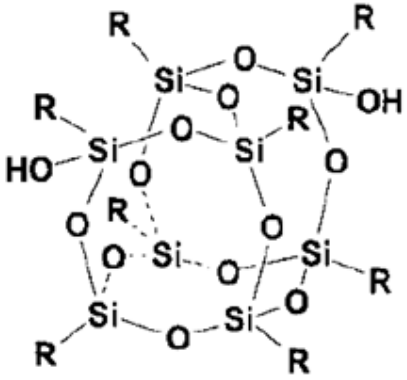
(c) T8



(d)T10



(e)T12

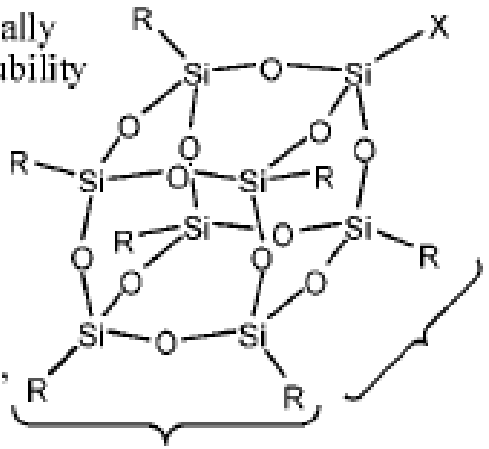


(f)Partial cage structure

Polyhedral Oligomeric Silsesquioxanes (POSS)

Unreactive R groups, usually organic, for stability, solubility and compatibility

One or more reactive X group (may be the same as R) for further modification, grafting or polymerisation



Nanoscale dimensions
Si···Si ca. 0.5 nm cage diagonal
R···R diagonal distance ca. 1 nm, for R = Me

Thermally and chemically robust organic-inorganic framework

Well defined, three-dimensional structure for introduction into polymers and composite materials

- excellent surface properitiess (silicon polymer)
- remarkable film-forming properties (polymers)
- high thermal stability and chemical resistance (POSS)

- microphase separation
- self-assembly behavor in the selected solution
- adhensive strength control

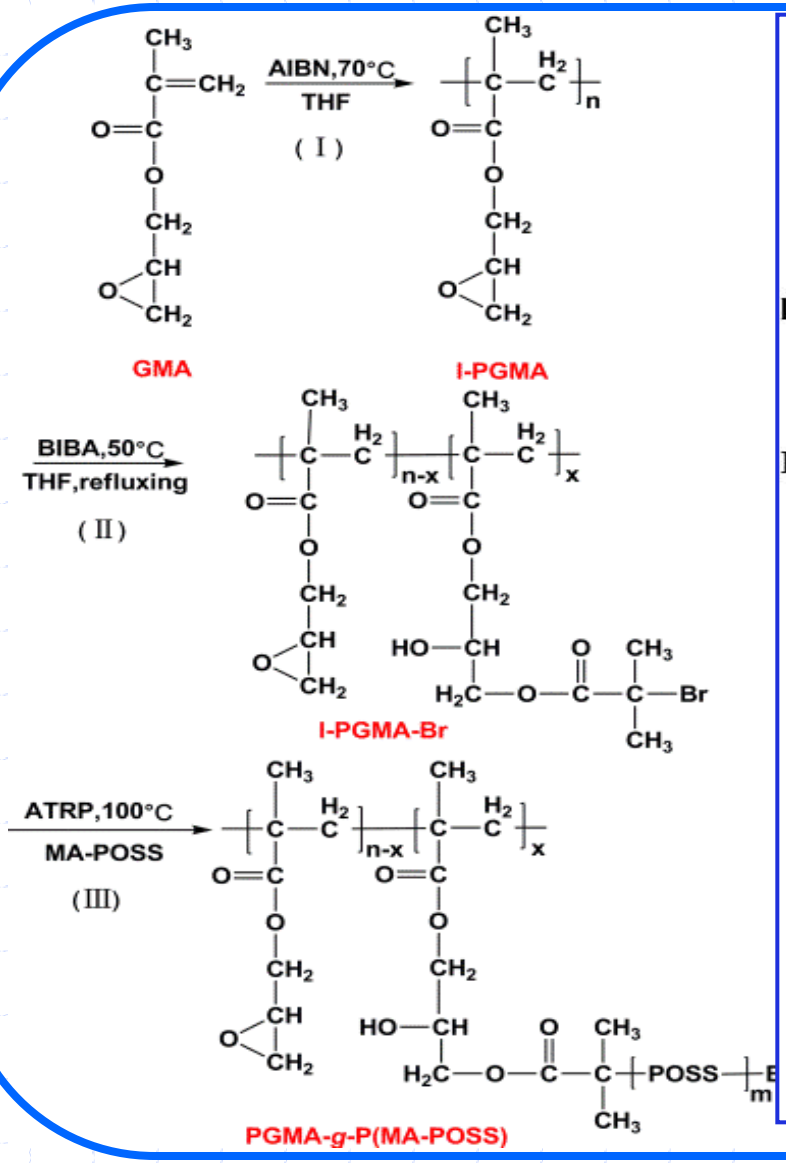
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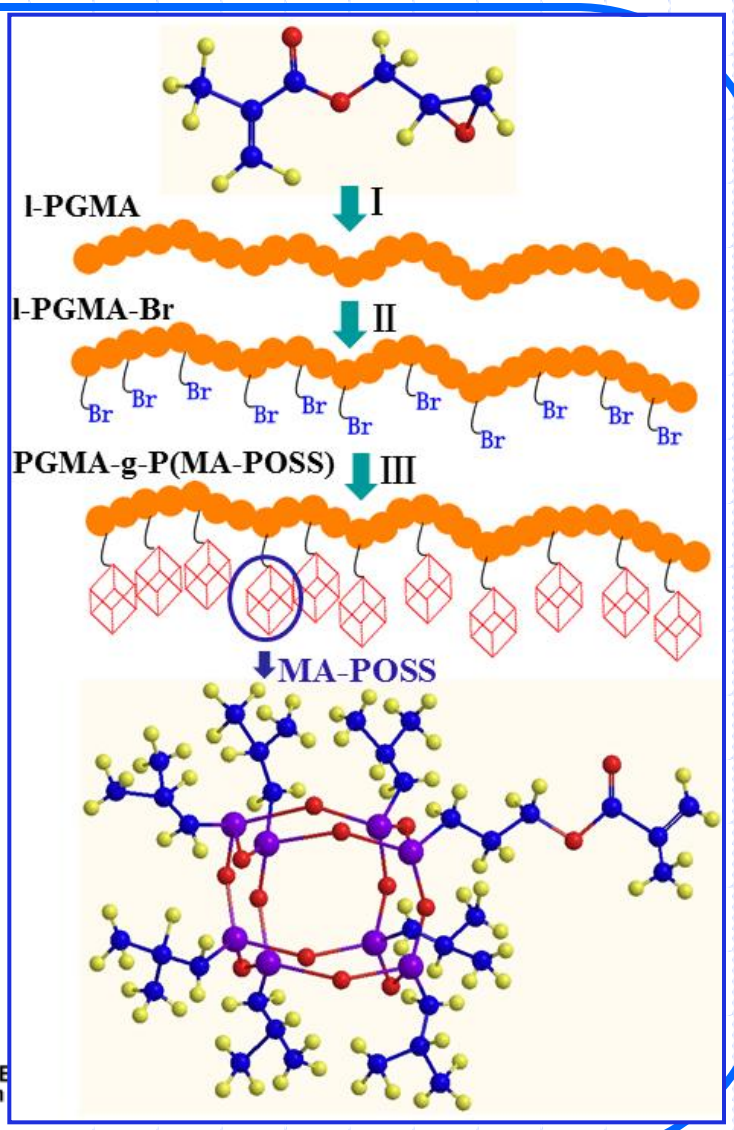
1 Background of protective requirement and POSS-based materials

2 Fabricatiion POSS-based materials for conservation of artworks

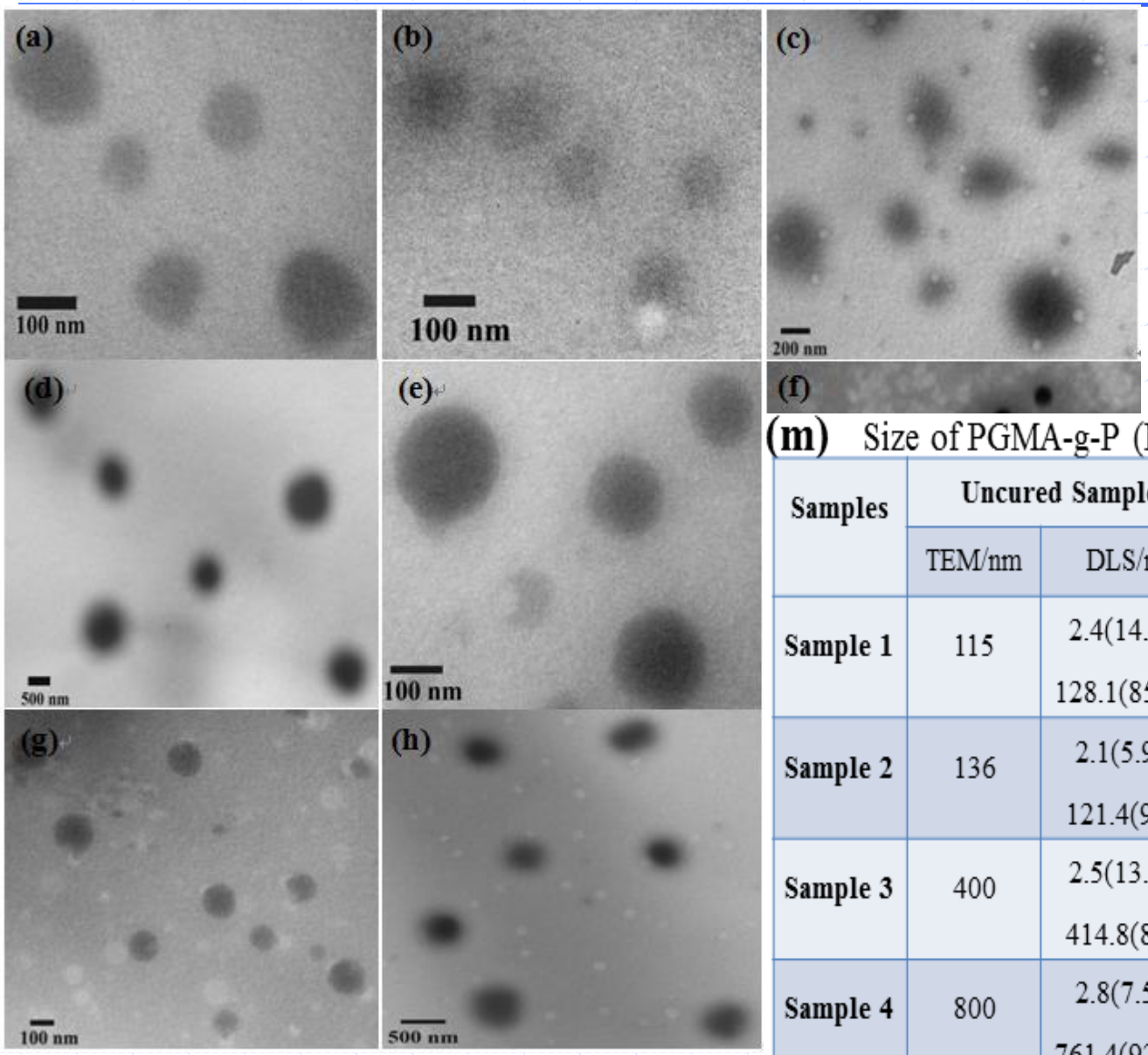
3 Evaluation of protective performance

2.1 PGMA-*g*-P(MA-POSS)





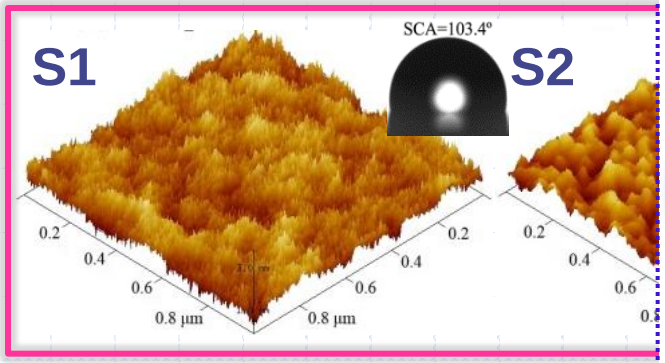
The TEM pictures of uncured Sample 1-4 (a-d), cured Sample 1-4 (e-h)
and the size distribution table of PGMA-g-P(MA-POSS) in THF solution (m)

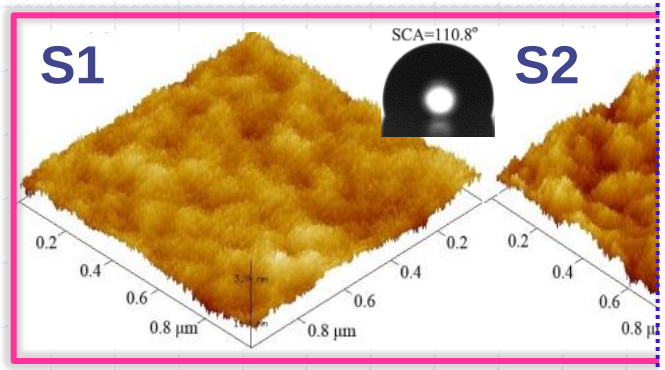


(m) Size of PGMA-g-P (MA-POSS) in THF solution

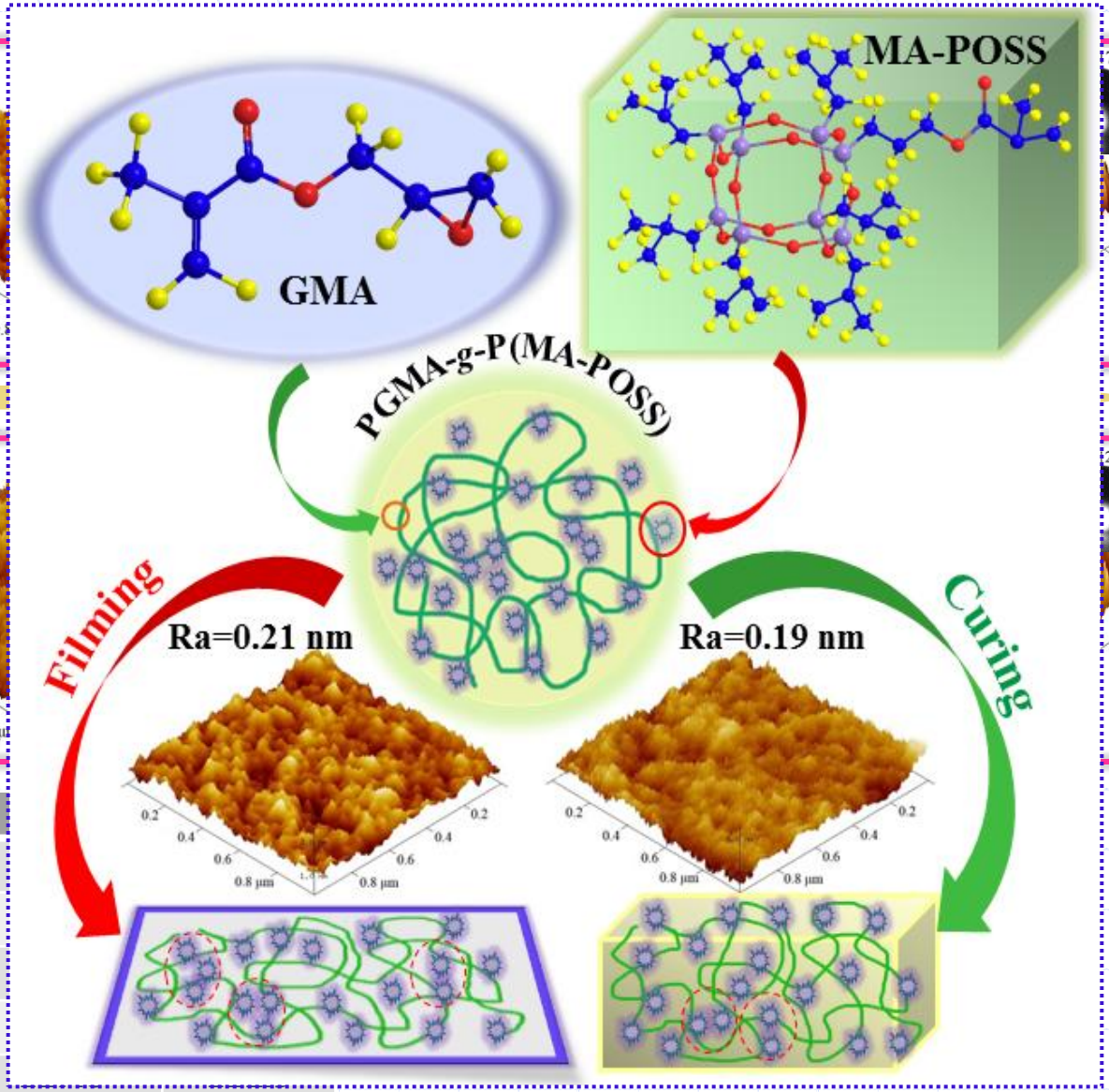
Samples	Uncured Samples		Cured Samples	
	TEM/nm	DLS/nm	TEM/nm	DLS/nm
Sample 1	115	2.4(14.8%) 128.1(85.2%)	167	5.1(9.3%) 172.0(90.7%)
Sample 2	136	2.1(5.9%) 121.4(94.1)	60	3.8(13.2%) 62.6(86.8%)
Sample 3	400	2.5(13.6%) 414.8(86.4)	145	4.4(12.4%) 165.4(87.6%)
Sample 4	800	2.8(7.5%) 761.4(92.5%)	600	5.8(8.7%) 643.9(91.3%)

Surface properties of PGMA-*g*-P(MA-POSS) film

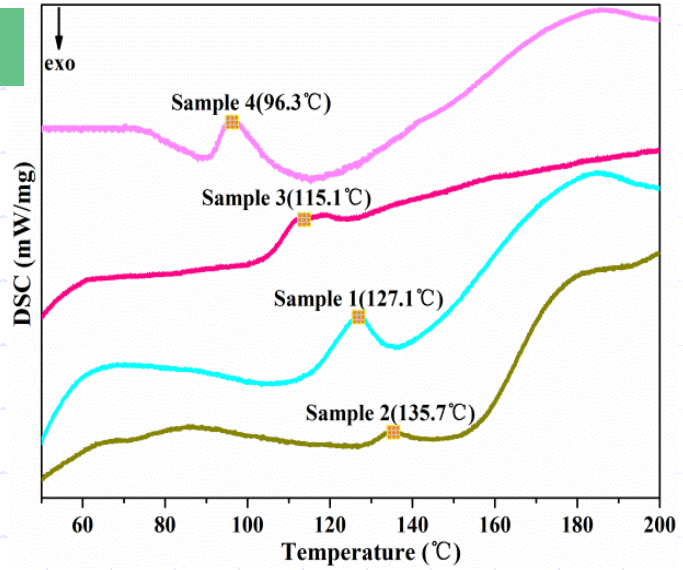




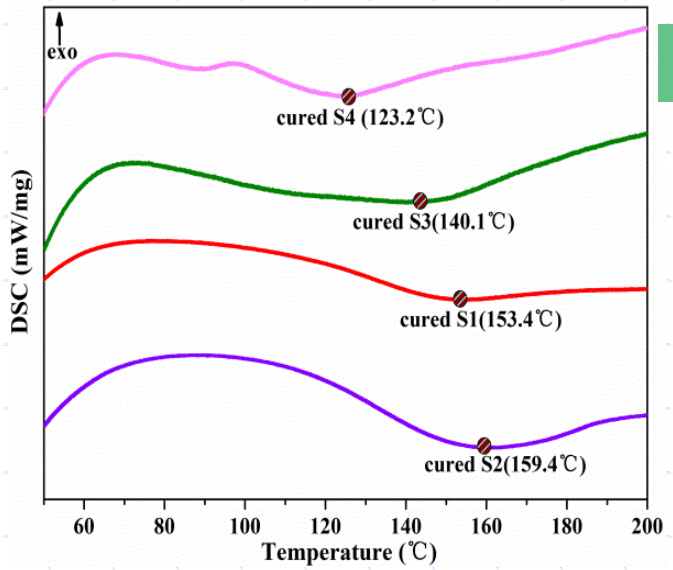
Sample	before	after
	Ra/nm	
S1	0.19	0.14
S2	0.21	0.19
S3	0.33	0.63
S4	4.1	14.4



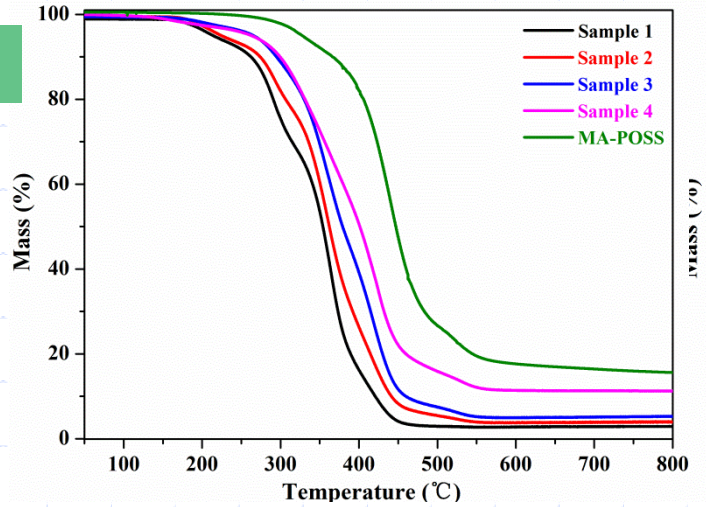
(a)


exo
Sample 4(96.3℃)
Sample 3(115.1℃)
Sample 1(127.1℃)
Sample 2(135.7℃)
DSC (mW/mg)
60
80
100
120
140
160
180
200
Temperature (℃)

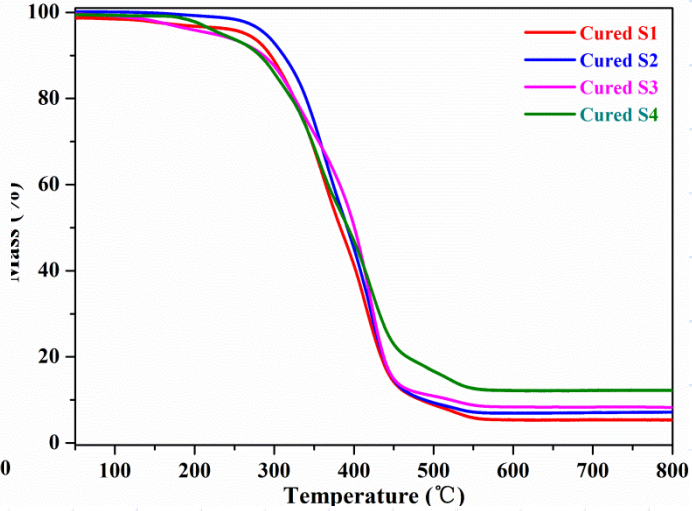
(b)

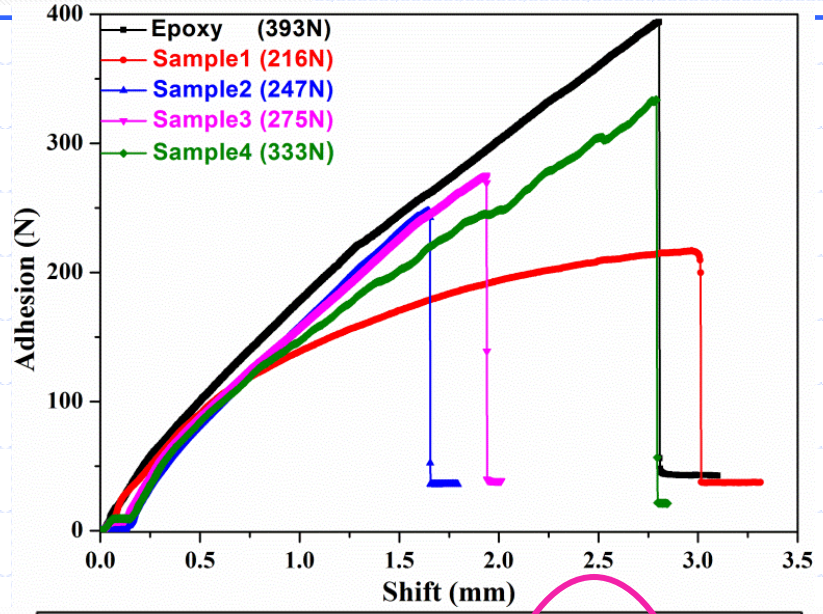

exo
cured S4 (123.2℃)
cured S3(140.1℃)
cured S1(153.4℃)
cured S2(159.4℃)
DSC (mW/mg)
60
80
100
120
140
160
180
200
Temperature (℃)

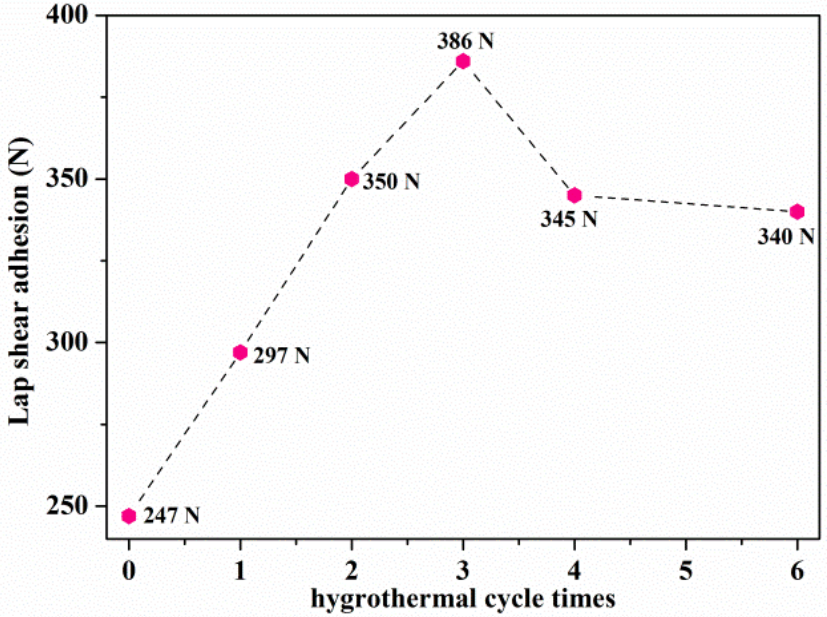
(c)

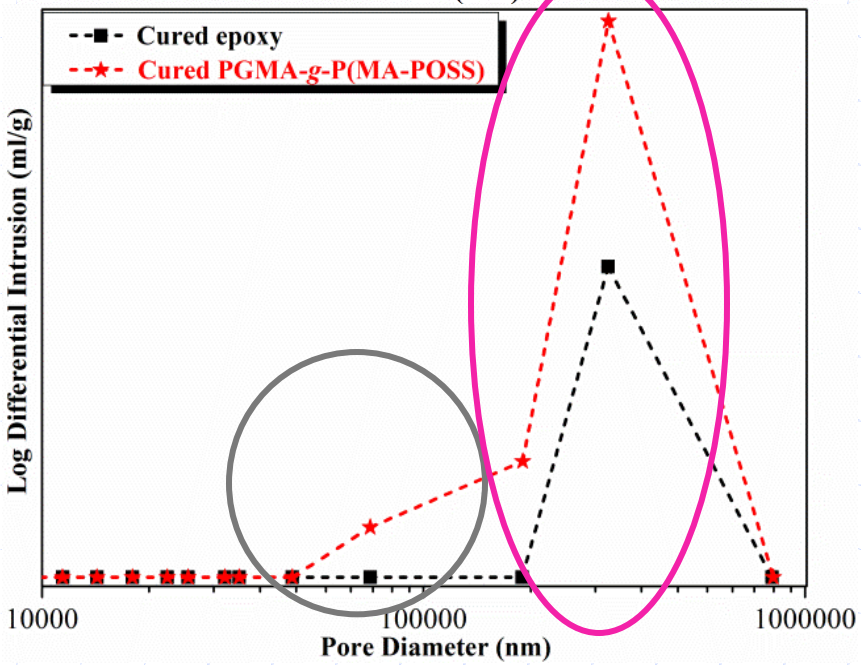

Sample 1
Sample 2
Sample 3
Sample 4
MA-POSS
Mass (%)
0
20
40
60
80
100
100
200
300
400
500
600
700
800
Temperature (℃)

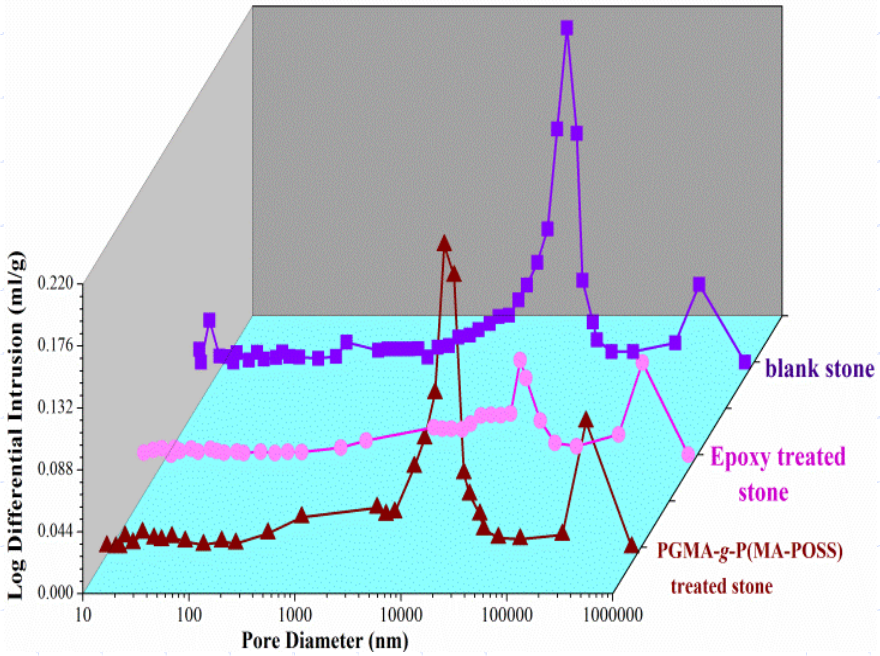
(d)


Cured S1
Cured S2
Cured S3
Cured S4
0
20
40
60
80
100
100
200
300
400
500
600
700
800
Temperature (℃)

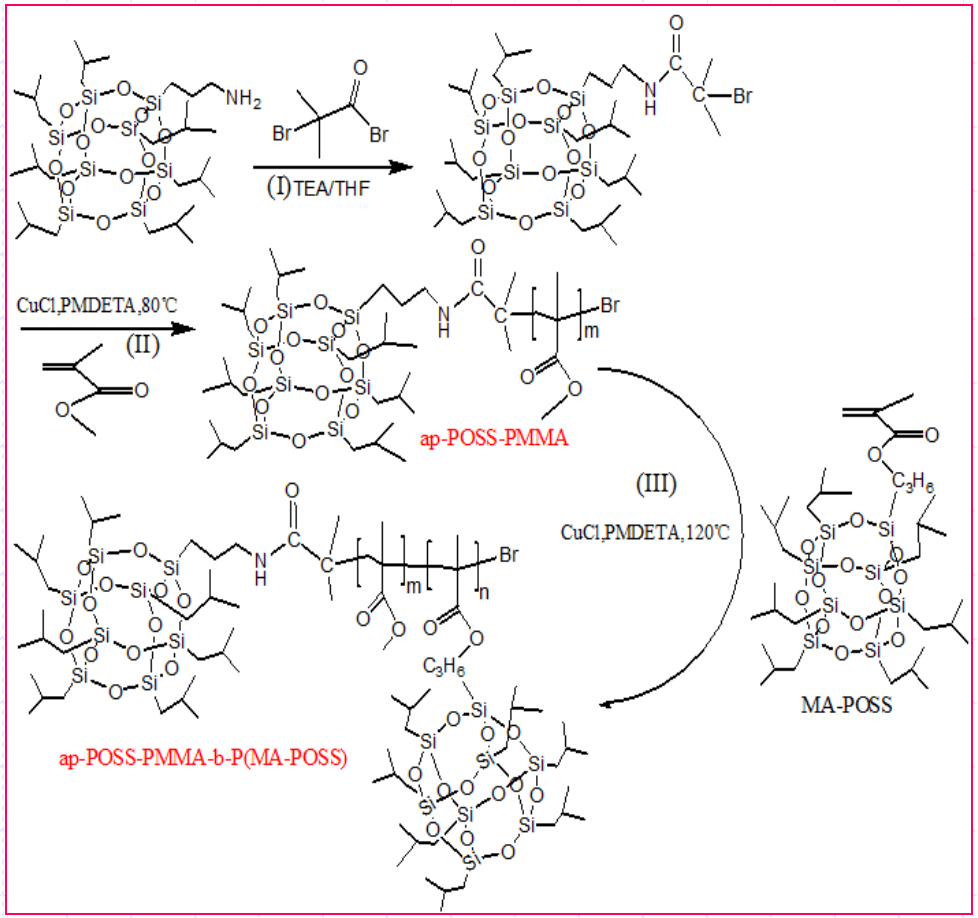

Epoxy (393N)
Sample1 (216N)
Sample2 (247N)
Sample3 (275N)
Sample4 (333N)
Adhesion (N)
Shift (mm)

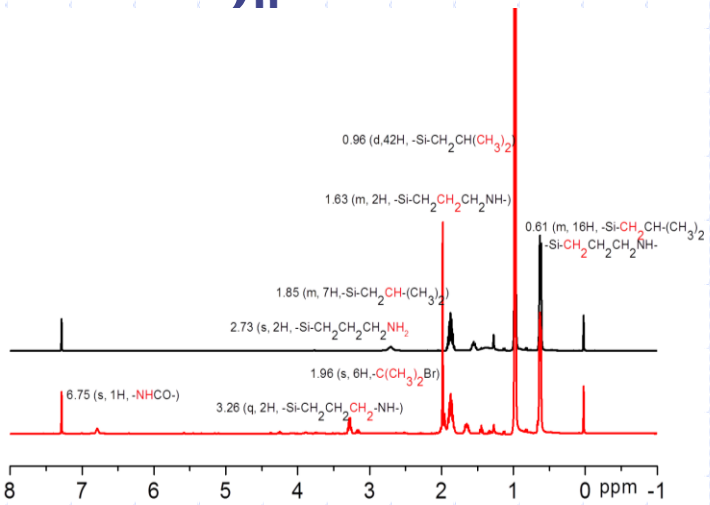

386 N
350 N
345 N
340 N
297 N
247 N
Lap shear adhesion (N)
hygrothermal cycle times

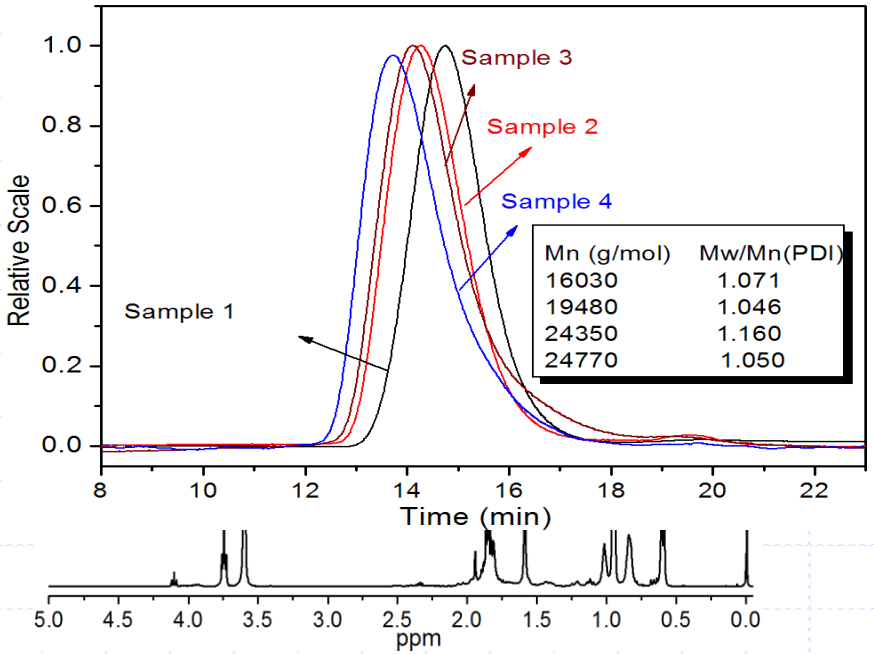

Cured epoxy
Cured PGMA-g-P(MA-POSS)
Log Differential Intrusion (ml/g)
Pore Diameter (nm)


blank stone
Epoxy treated stone
PGMA-g-P(MA-POSS) treated stone
Log Differential Intrusion (ml/g)
Pore Diameter (nm)

2.2 *ap*-POSS-PMMA$_m$-b-P(MA-POSS)$_n$







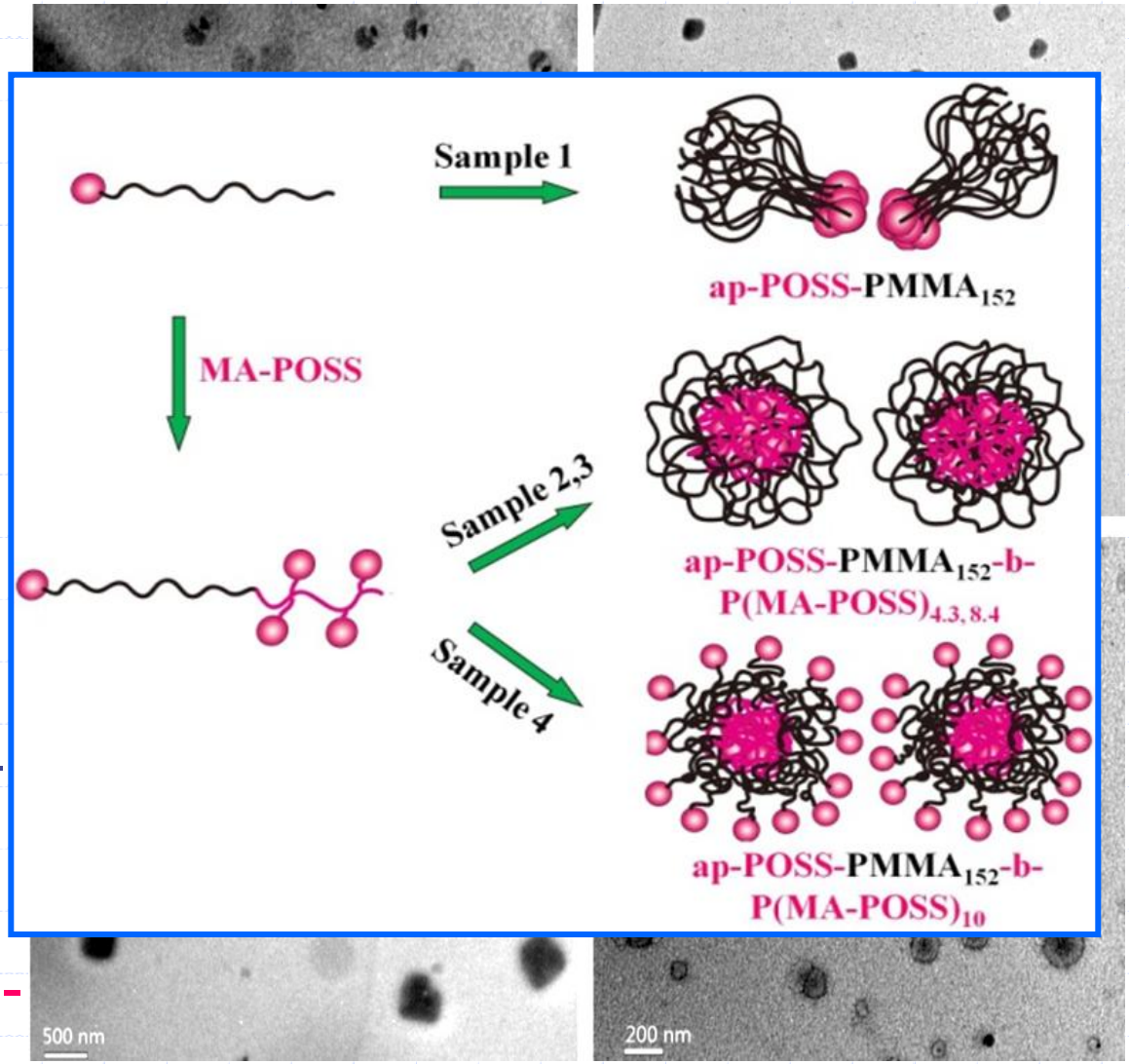
2.2 *ap*-POSS-PMMA$_m$-b-P(MA-POSS)$_n$

Sample 1: *ap*-POSS-PMMA$_m$ **155nm shovel-shape**

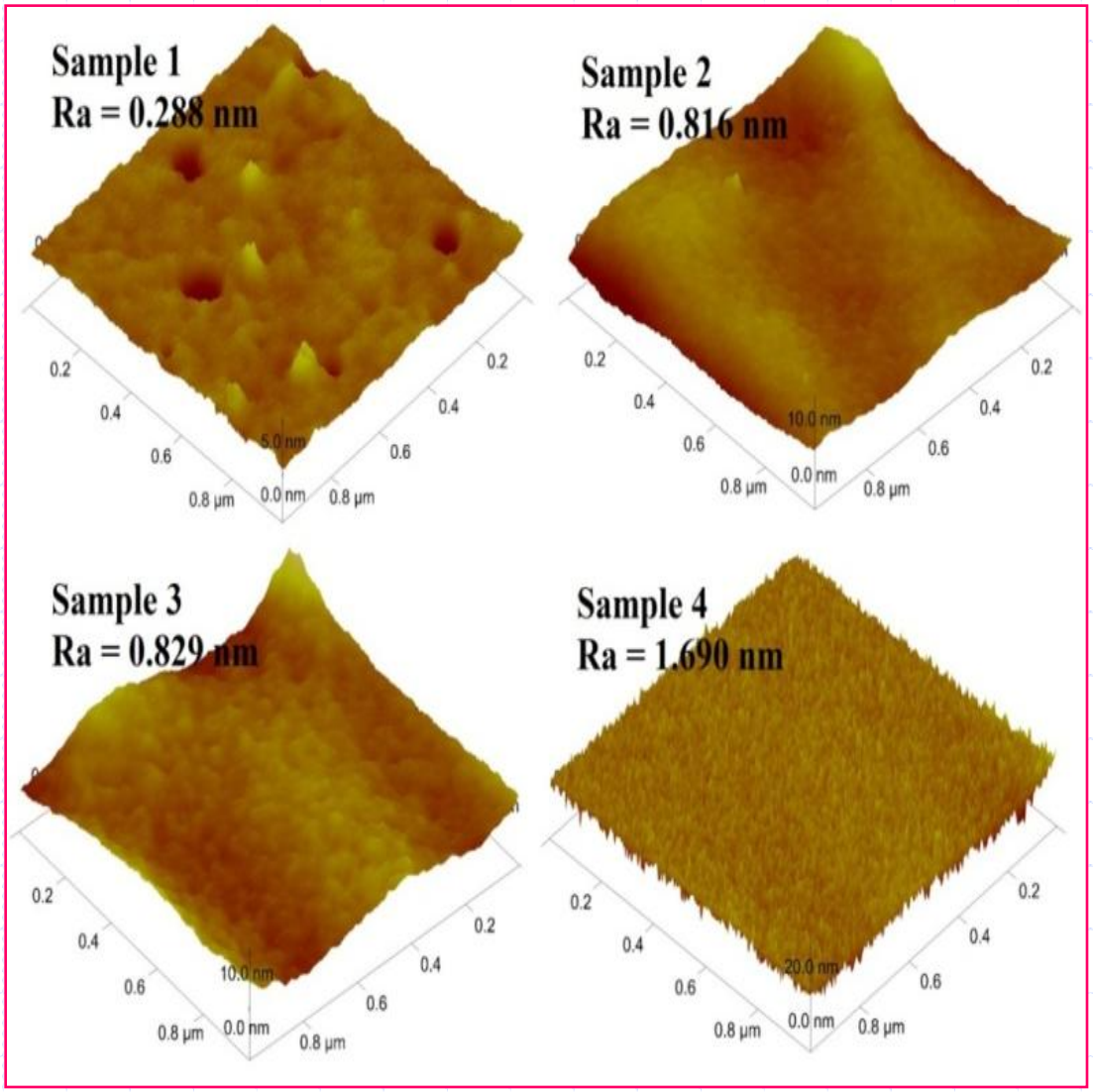
Sample 2: *ap*-POSS-PMMA$_m$-b-P(MA-POSS)$_{4.3}$ **195nm core-shell**

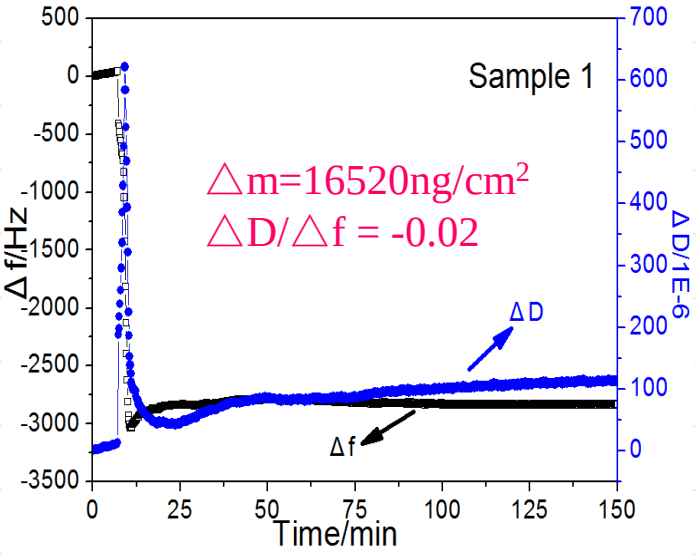
Sample 3: *ap*-POSS-PMMA$_m$-b-P(MA-POSS)$_{8.4}$ **295nm core-shell**

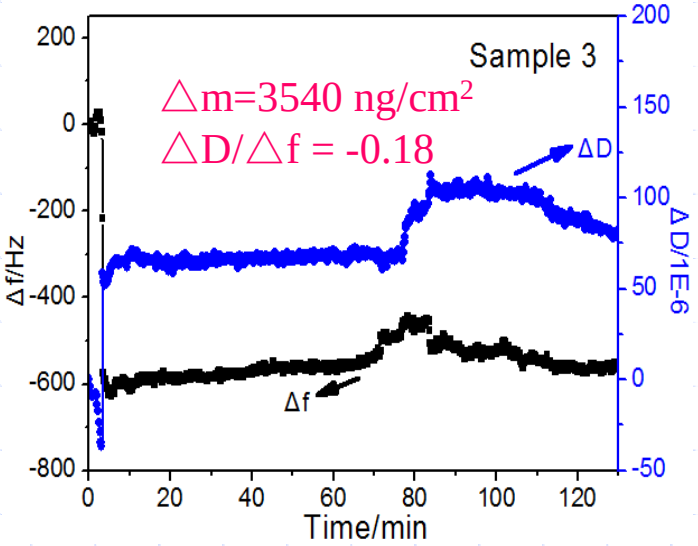
Sample 4: *ap*-POSS-PMMA$_m$-b-P(MA-POSS)$_{10.0}$ **159nm core-shell-crown**



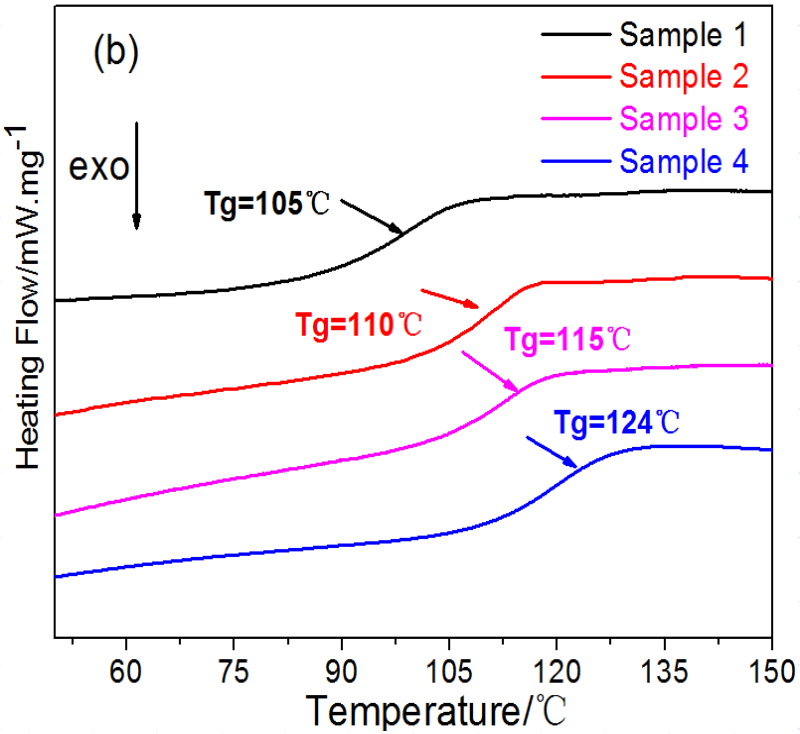
2.2 *ap*-POSS-PMMA$_m$-b-P(MA-POSS)$_n$

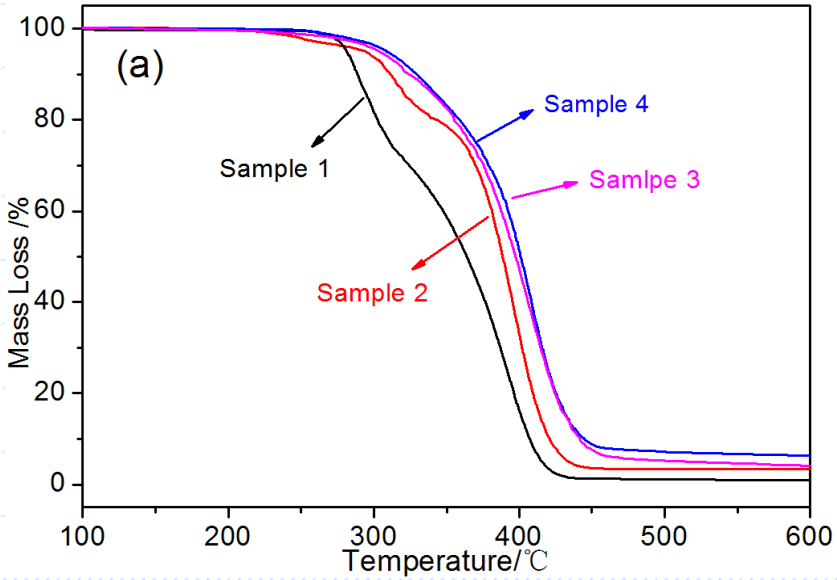


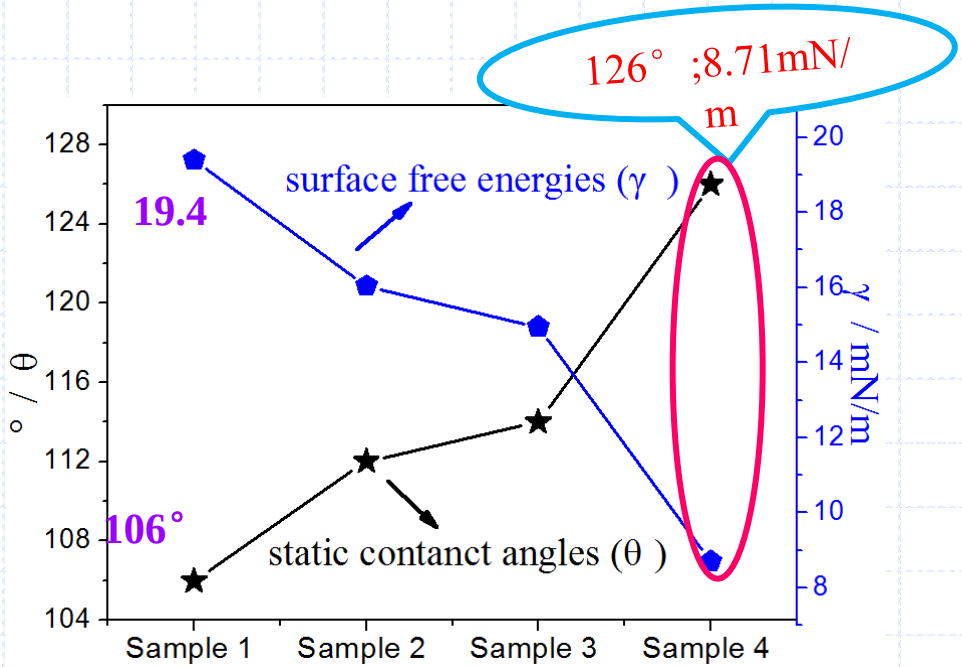




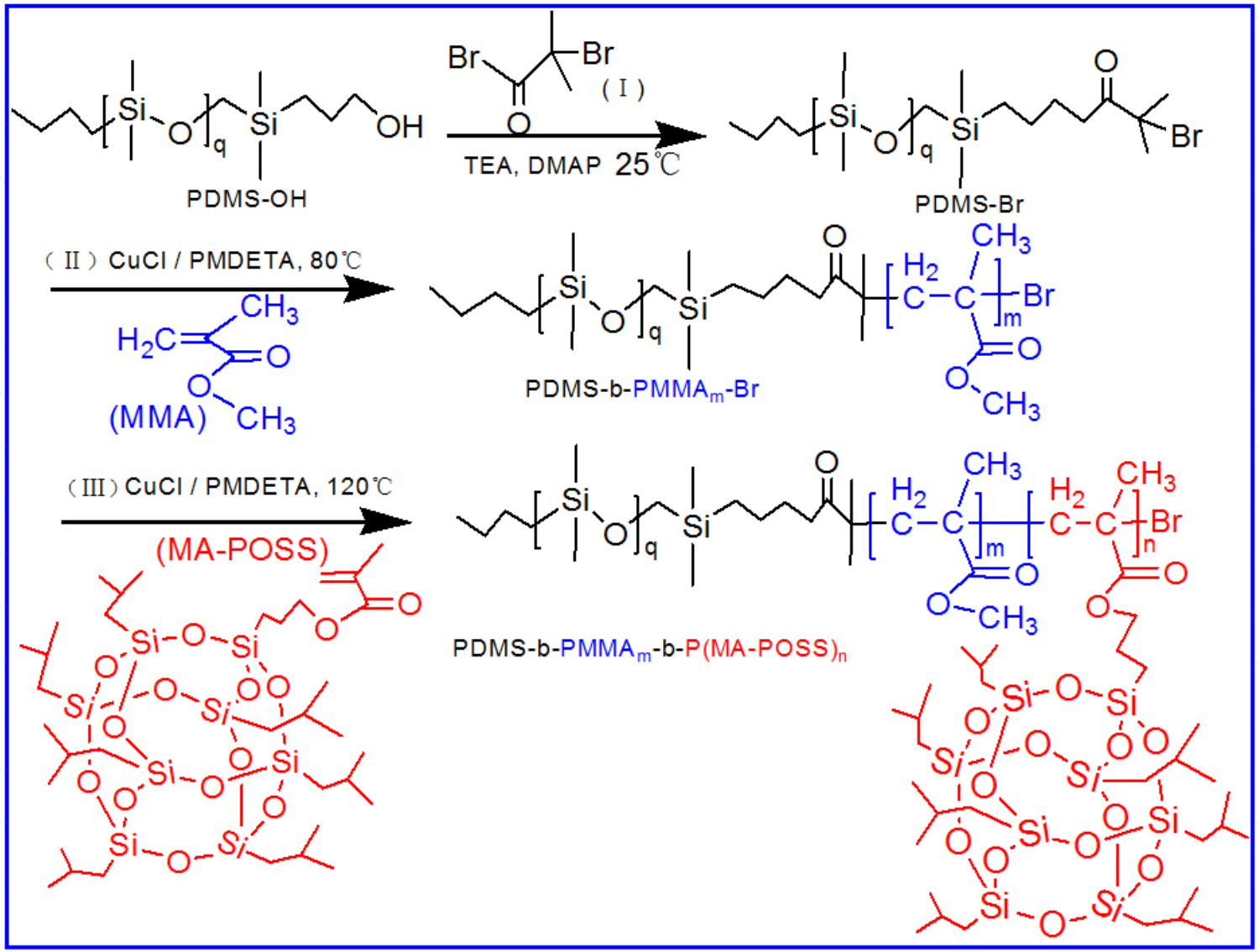
2.2 *ap*-POSS-PMMA$_m$-b-P(MA-POSS)$_n$



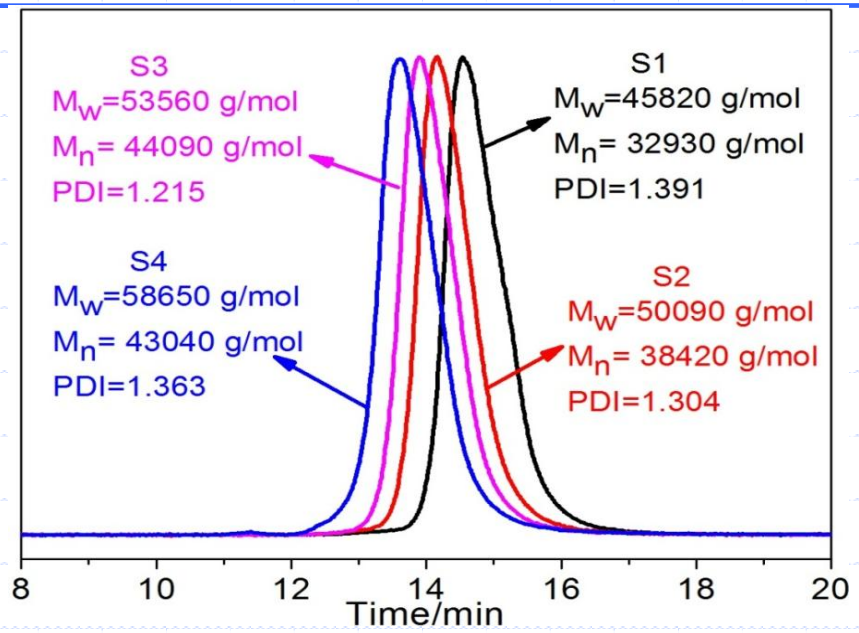


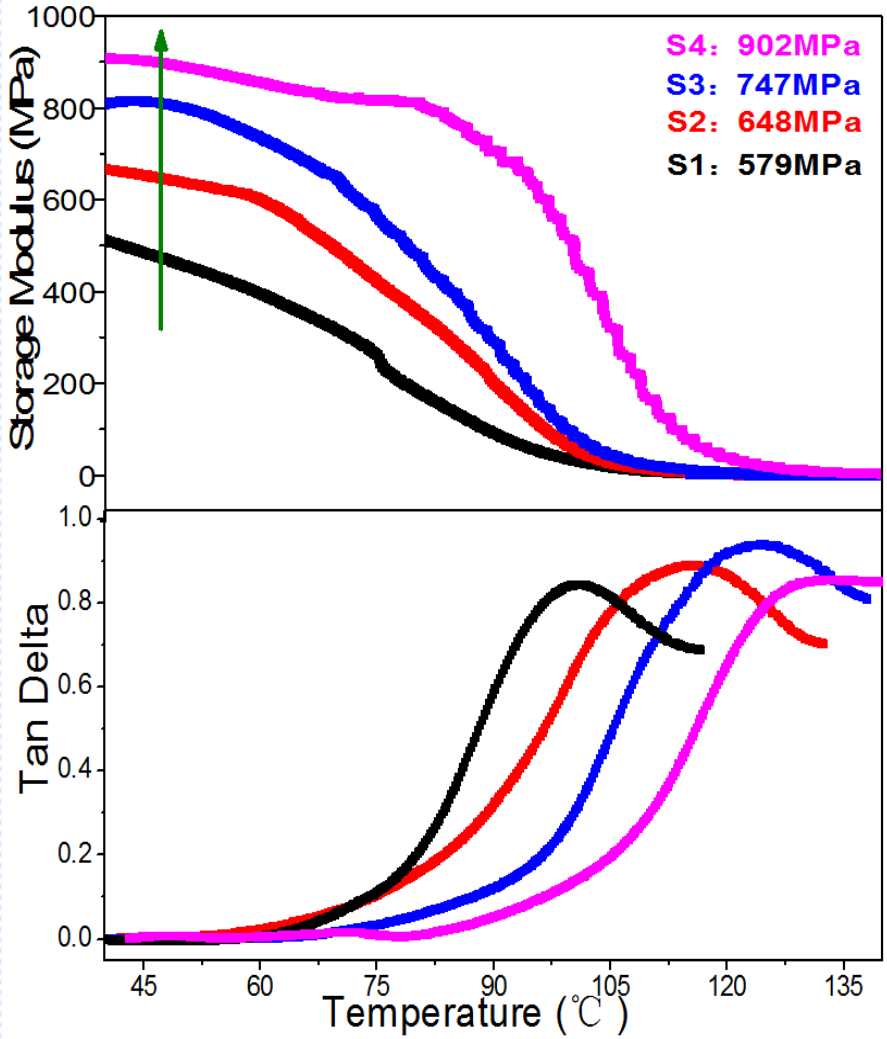


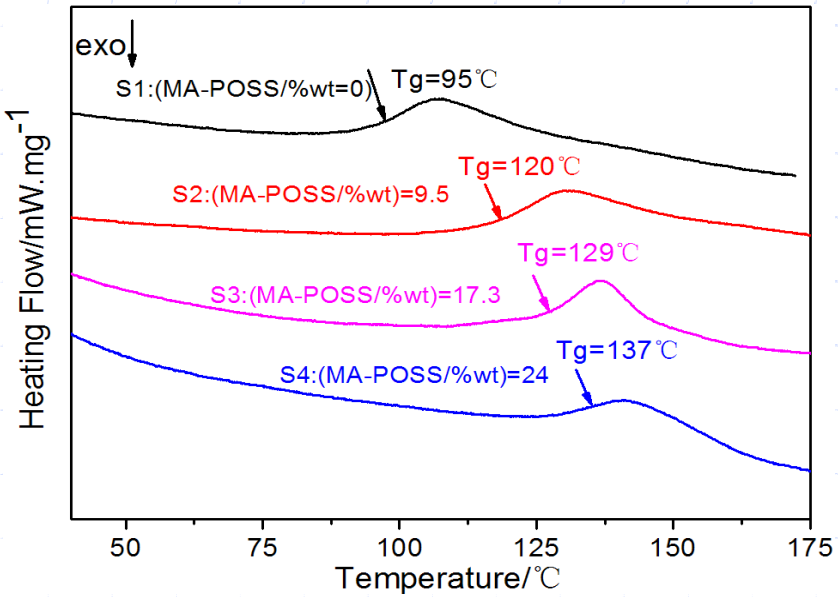
2.3 PDMS-b-PMMA$_m$-b-P(MA-POSS)$_n$

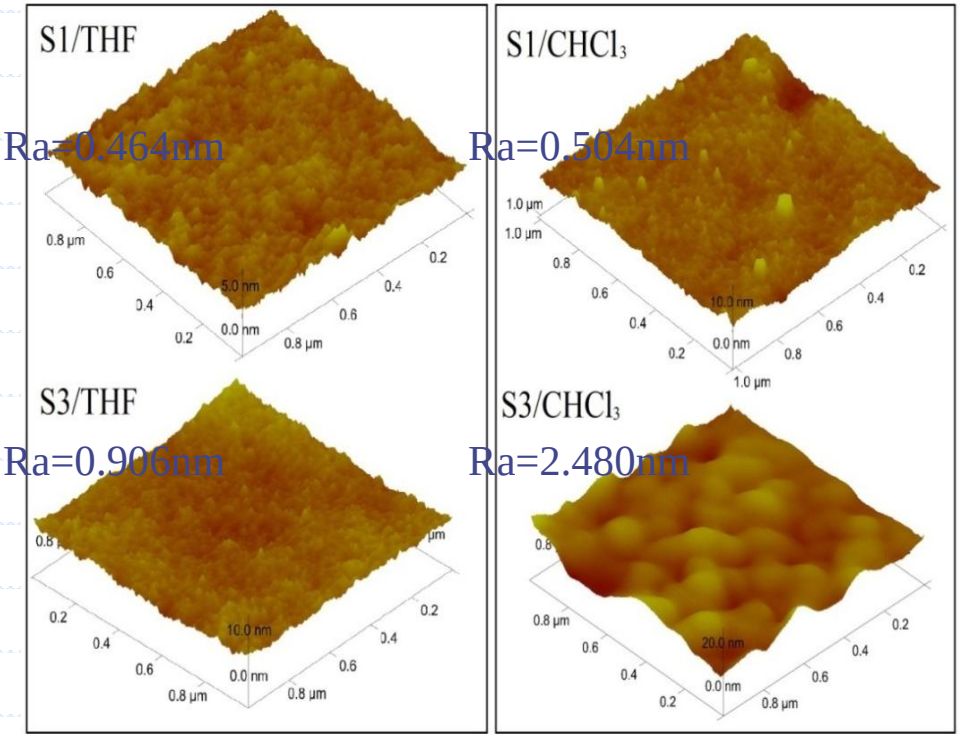


2.3 PDMS-b-PMMA$_m$-b-P(MA-POSS)$_n$

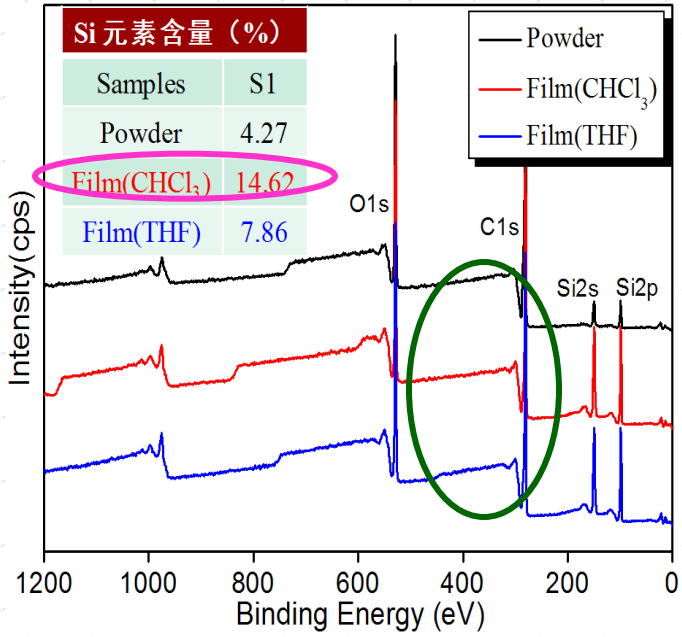


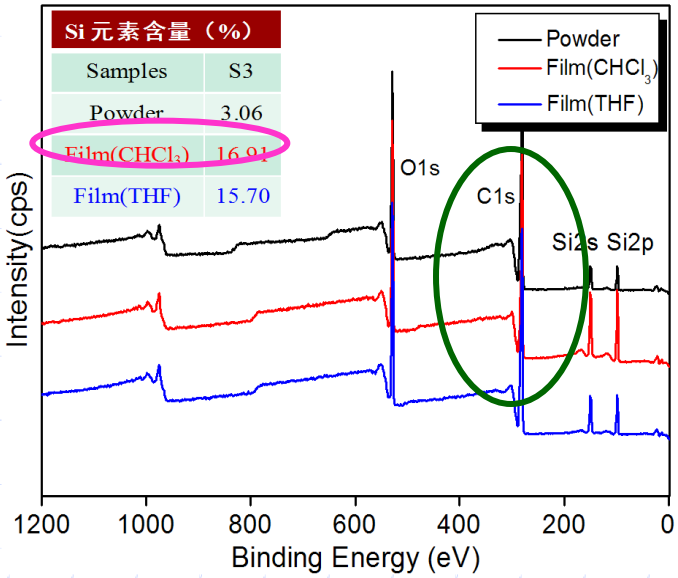


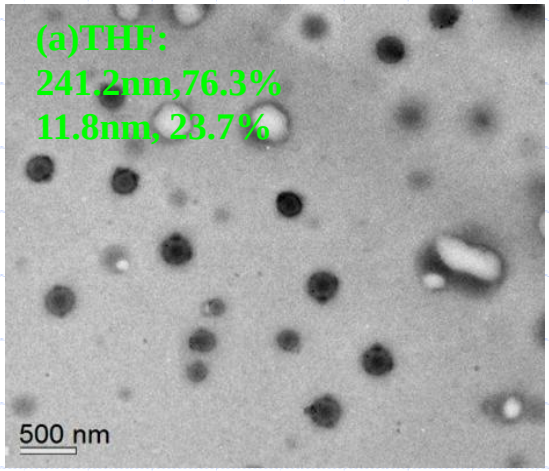


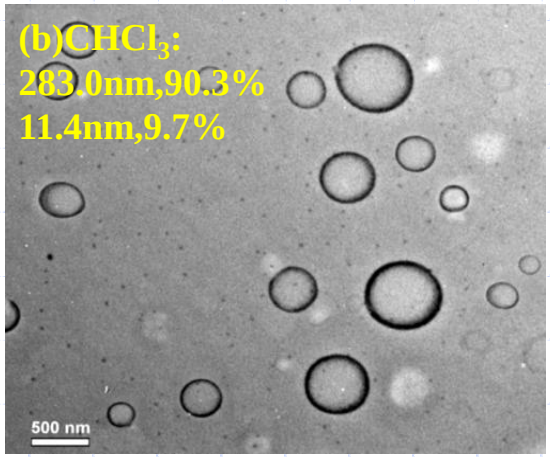


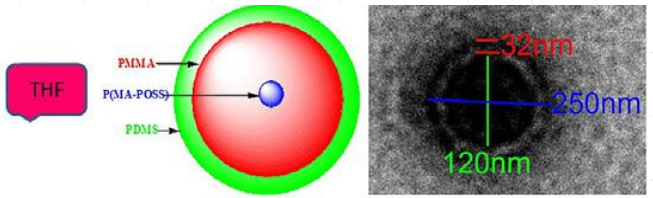
Code	Solvents	Θ_{H2O}	Θ_{Hex}	γ/mNm^{-1}
S1	THF	108°	20°	26.10
	$CHCl_3$	110°	22°	25.63
S3	THF	114°	26°	24.93
	$CHCl_3$	120°	32°	23.96

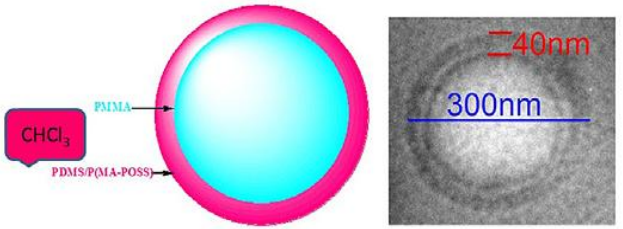


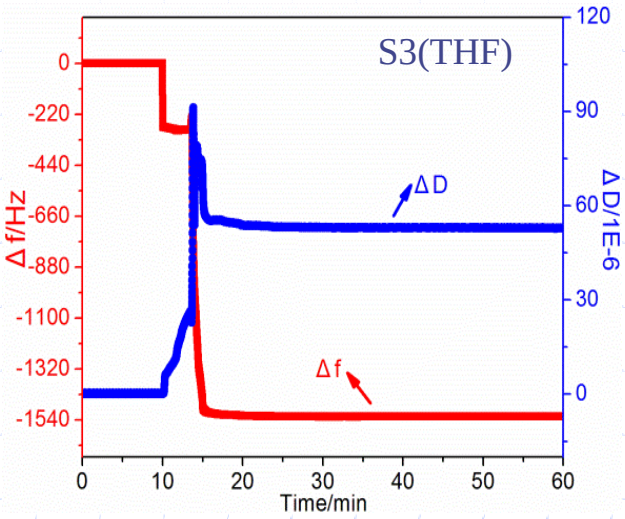




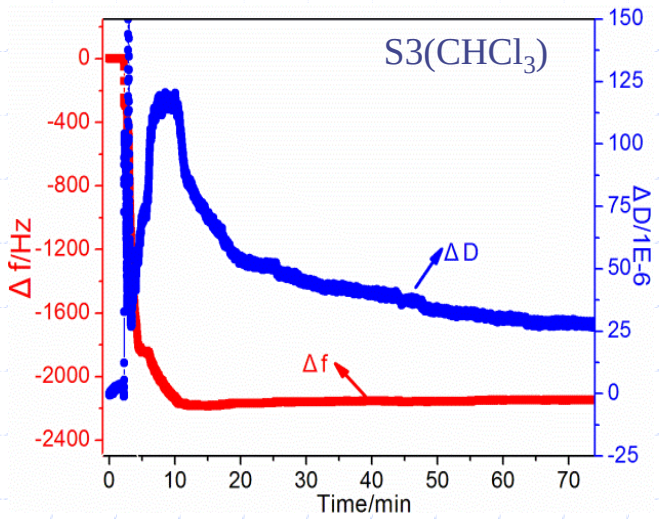








-1540Hz, 50×10^{-6}

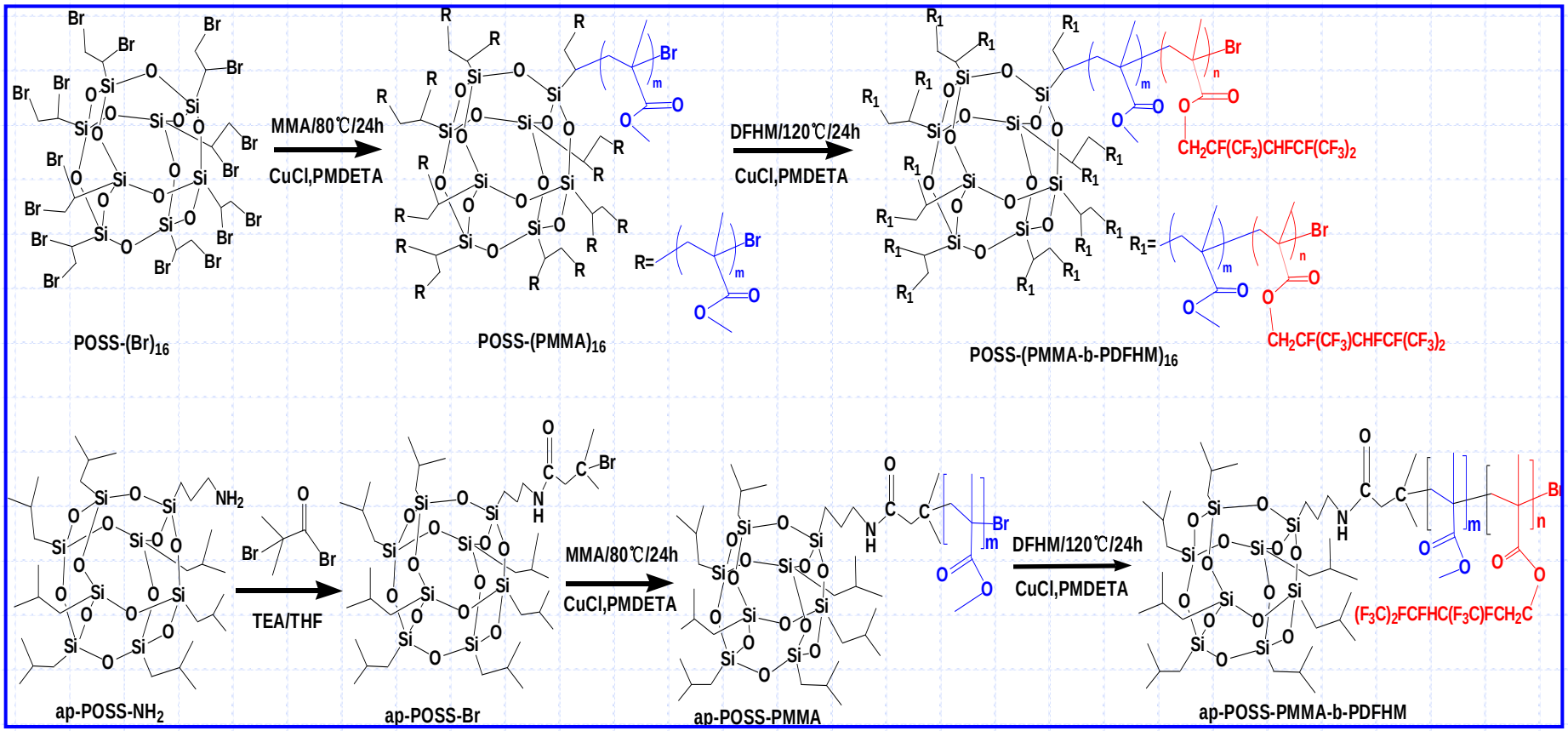


-2300Hz, 26×10^{-6}

$CHCl_3$ (Δf=-2300Hz) ($\Delta D=26\times10^{-6}$)

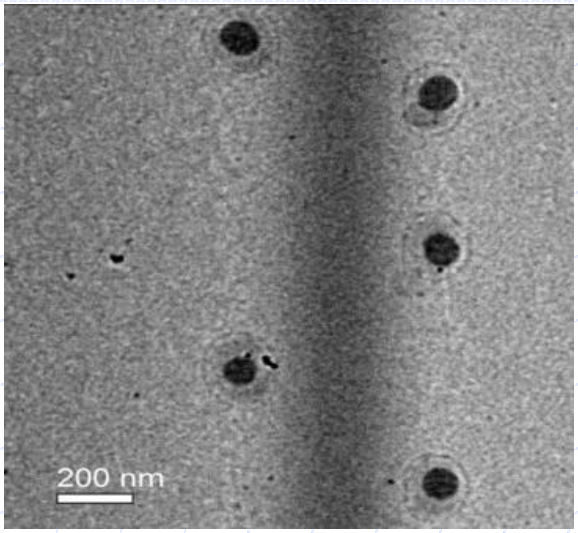
THF (Δf=-1540Hz, $\Delta D=52\times10^{-6}$)。

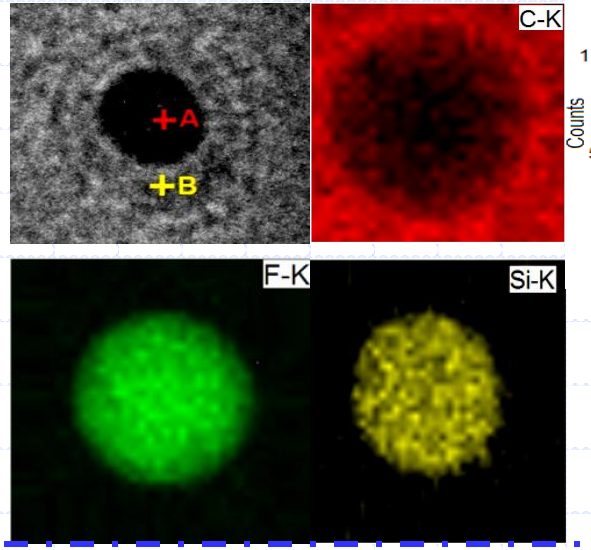
2.4 POSS-(PMMA-b-PDFHM)$_{16}$ and ap-POSS-PMMA-b-PDFHM

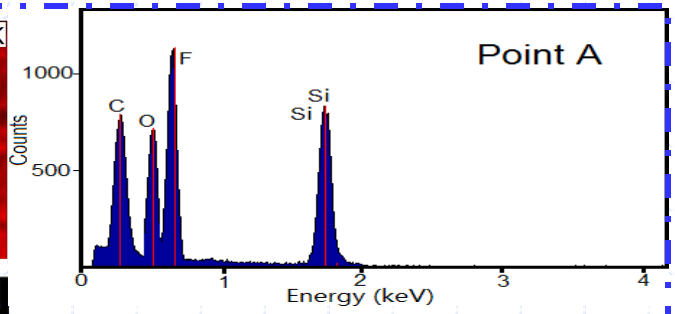


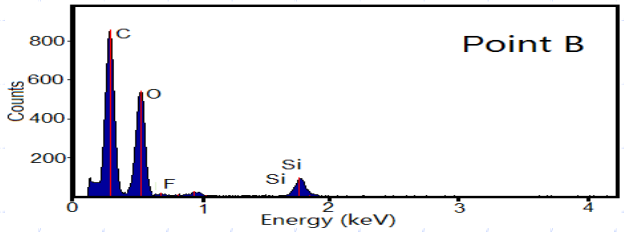
西安交通大学 XI'AN JIAOTONG UNIVERSITY

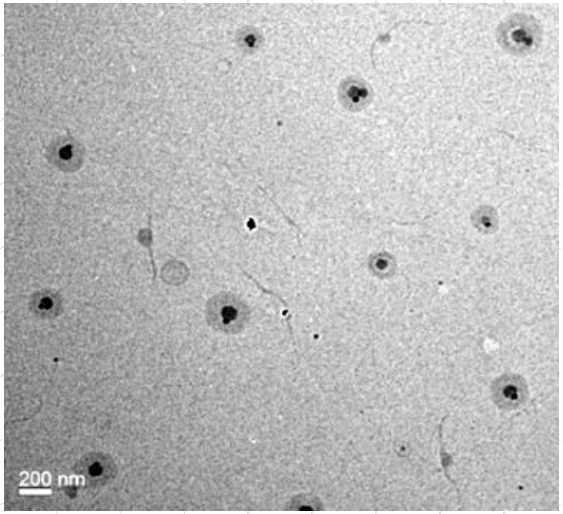
s-POSS-(PMMA-b-PDFHM)$_{16}$ 110 nm CS micelles

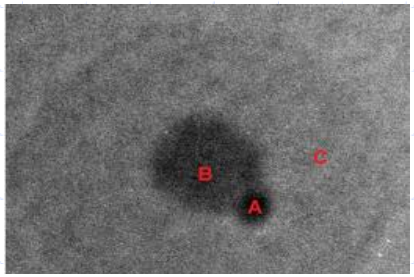


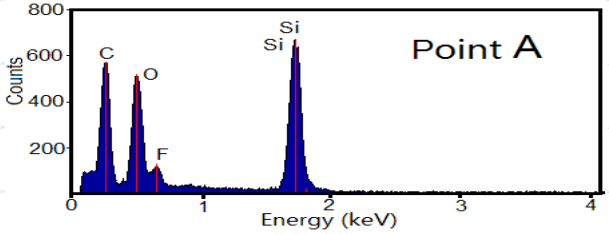


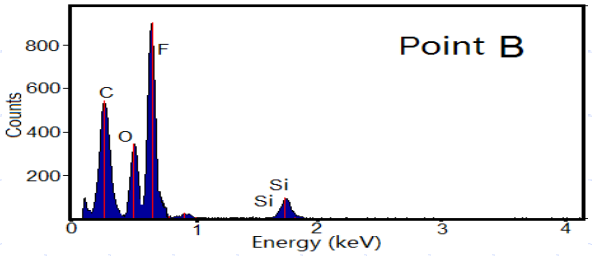


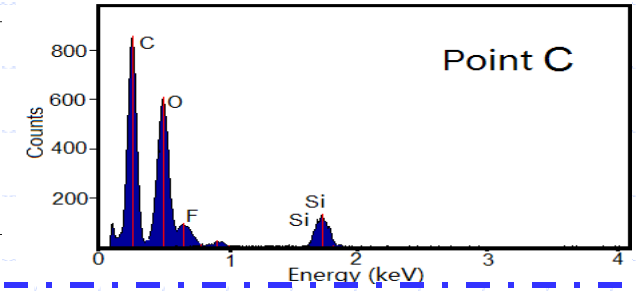






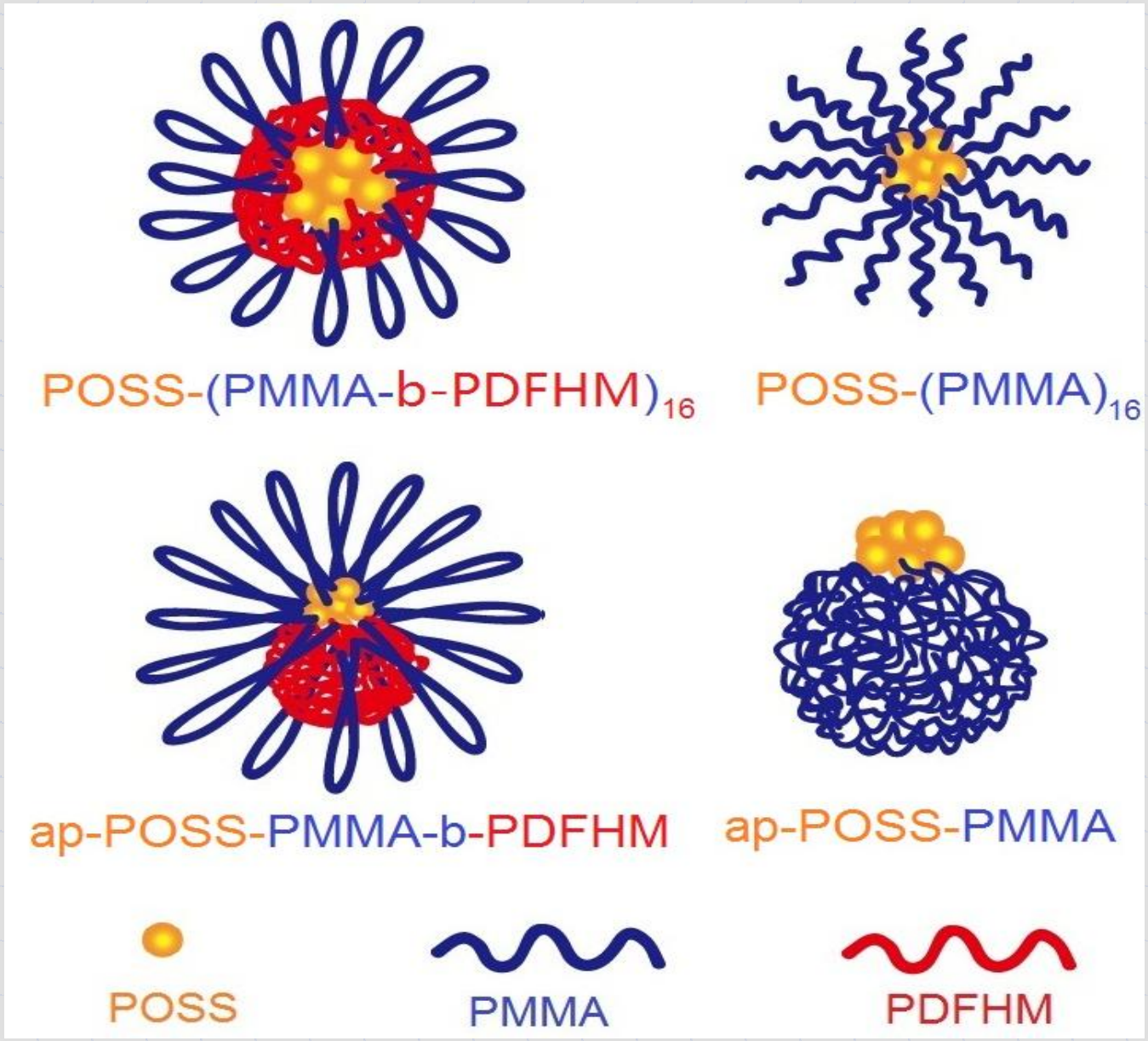


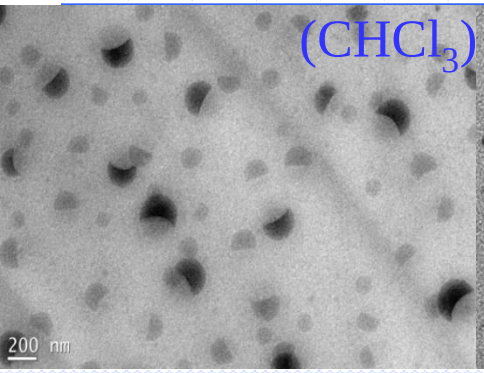


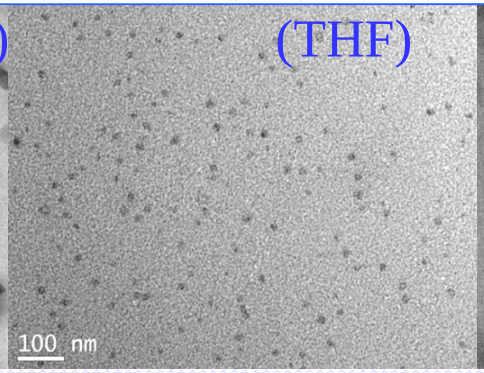


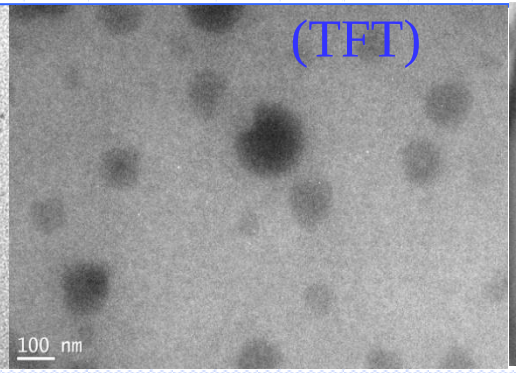
ap-POSS-PMMA-b-PDFHM 200 nm CS micelles

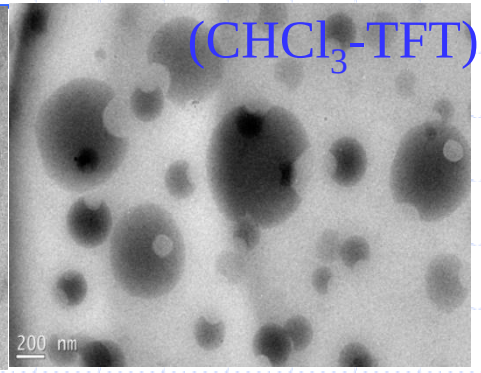
➢Self-assembled micelles

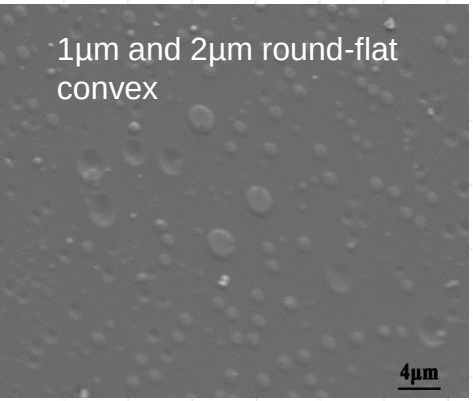


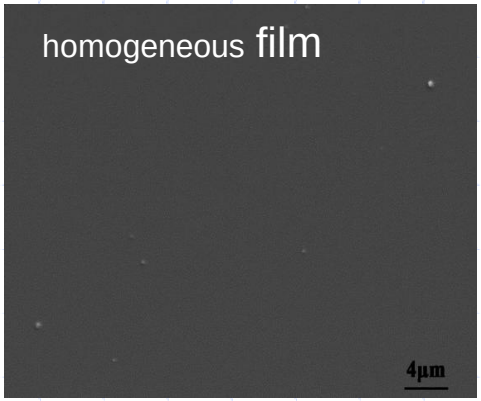


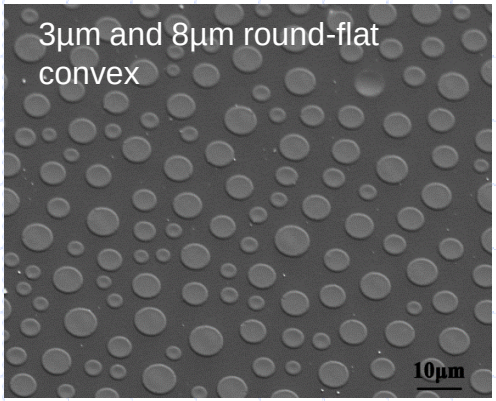


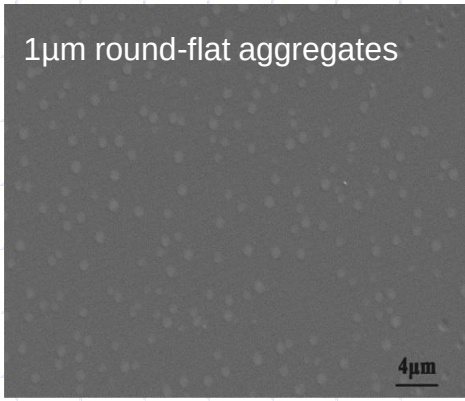


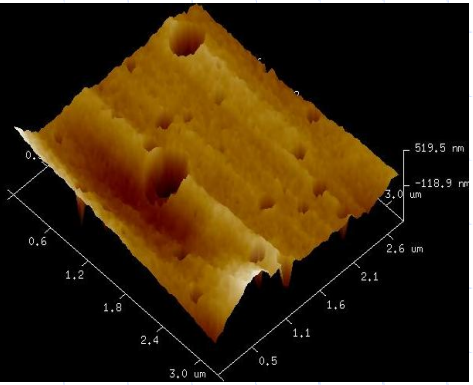


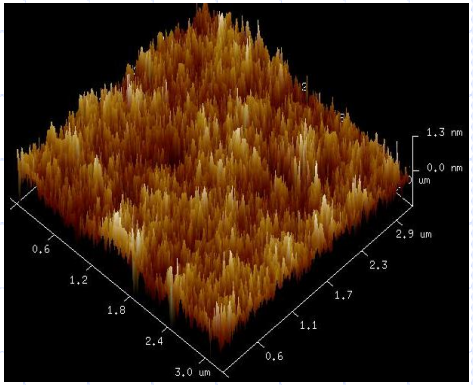


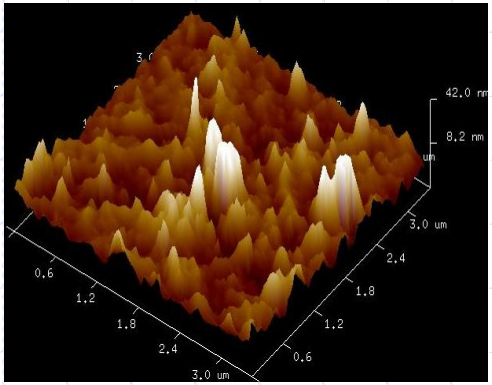


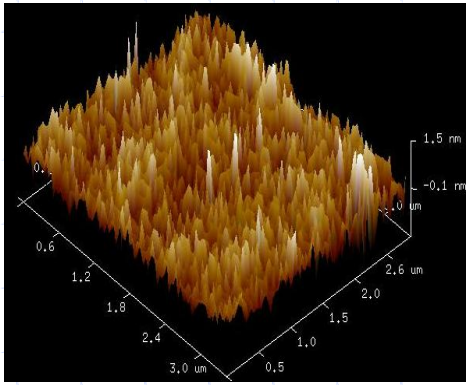












500 nm

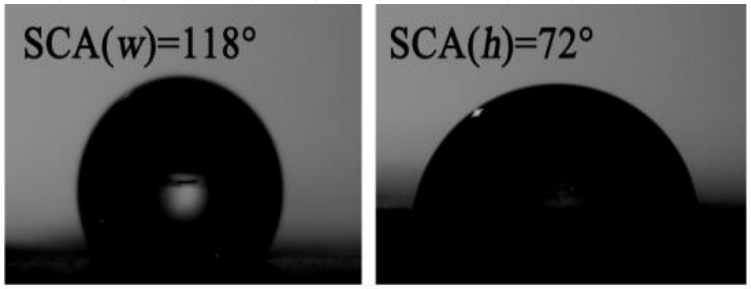
1.3 nm

42 nm

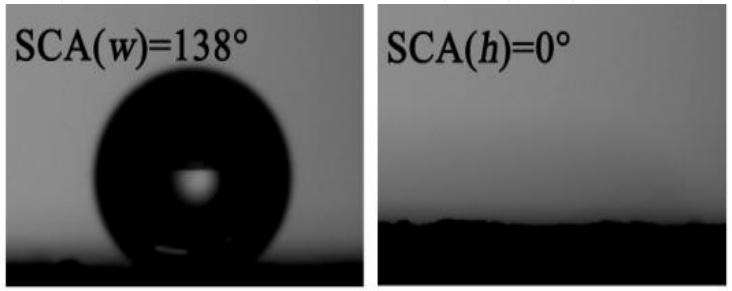
1.5 nm

➢Surface chemical composition

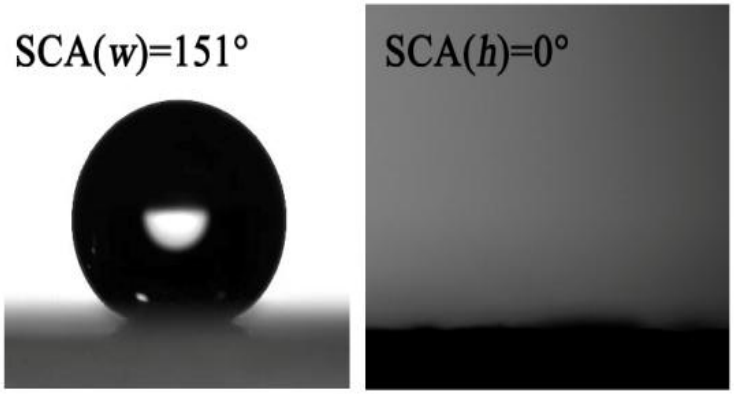
Copolymers	Samples	Surface roughness		Chemical composition/wt%			
		Ra/nm	RMSR/nm	C	O	F	Si
s-POSS-(PMMA-b-PDFHM)$_{16}$	Powder	-	-	47.80	36.18	15.05	0.97
	Film/THF	4.9	50.4	34.42	23.37	41.39	0.82
	Film/$CHCl_3$	6.1	82.8	29.21	23.22	52.34	0.09
	Film/DMC	3.6	36.3	33.99	29.56	35.21	1.24
ap-POSS-PMMA-b-PDFHM	Powder	-	-	51.37	37.85	9.81	0.97
	Film/THF	18.5	100.6	23.94	14.41	61.56	0.09
	Film/$CHCl_3$	23.6	143.0	24.32	15.31	60.34	0.03
	Film/DMC	4.0	68.8	36.28	27.35	34.39	1.98



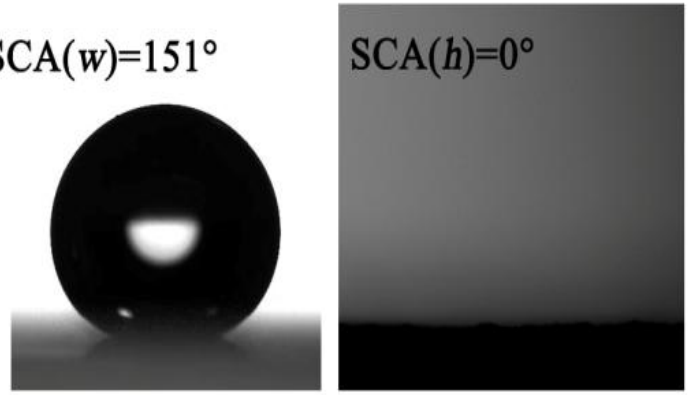
(a)



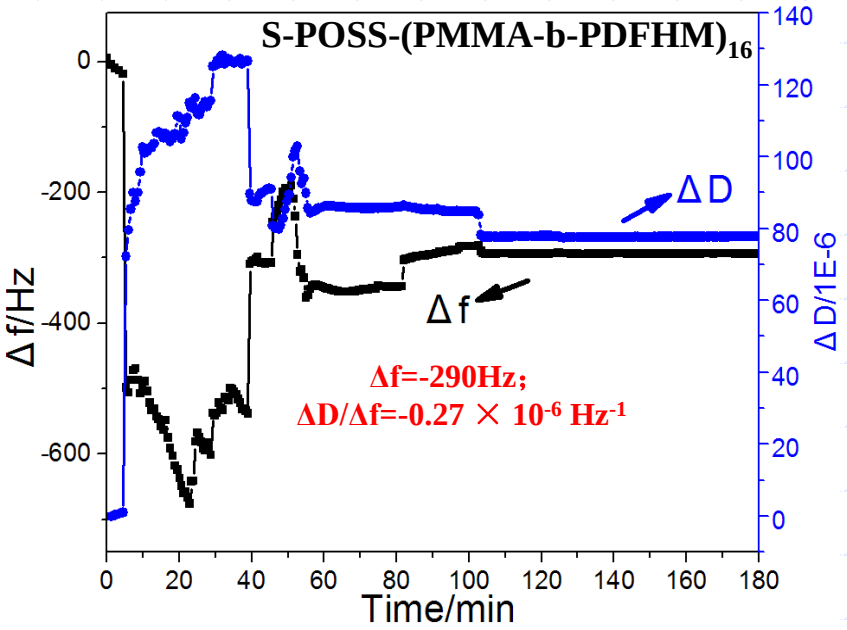
(b)

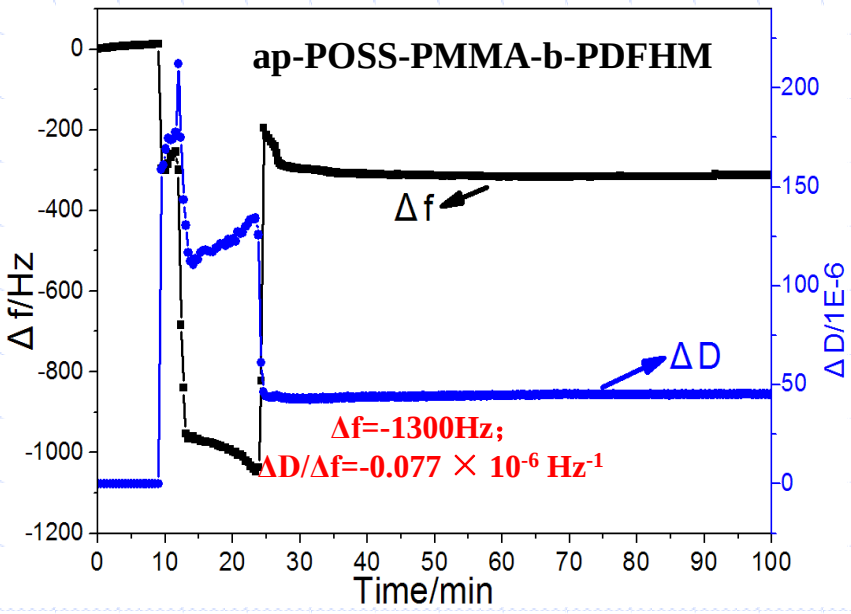


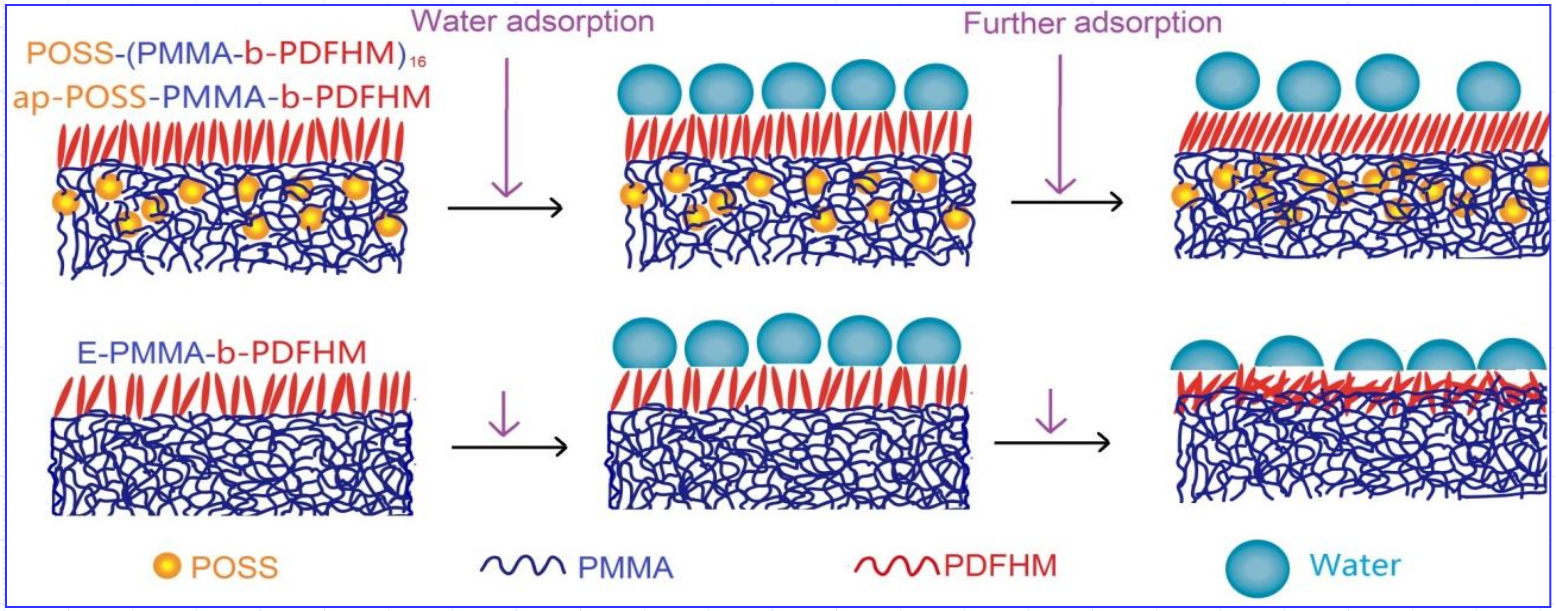
(c)



(d)


S-POSS-(PMMA-b-PDFHM)16
ΔD
Δf
Δf=-290Hz;
ΔD/Δf=-0.27 × 10-6 Hz-1
Δf/Hz
ΔD/1E-6
Time/min


ap-POSS-PMMA-b-PDFHM
Δf
ΔD
Δf=-1300Hz;
ΔD/Δf=-0.077 × 10-6 Hz-1
Δf/Hz
ΔD/1E-6
Time/min


Water adsorption
Further adsorption
POSS-(PMMA-b-PDFHM)16
ap-POSS-PMMA-b-PDFHM
E-PMMA-b-PDFHM
POSS
PMMA
PDFHM
Water

Contents

1 **Background of protective requirement and POSS-based materials**

2 **Fabricatiion POSS-based materials for conservation of artworks**

3 **Evaluation of protective performance**

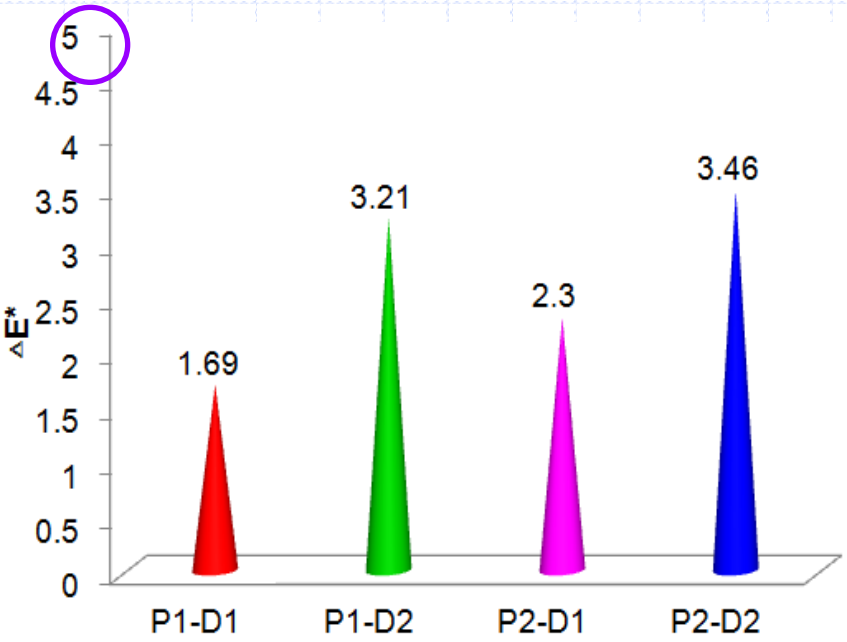
3.1 P1 and P2





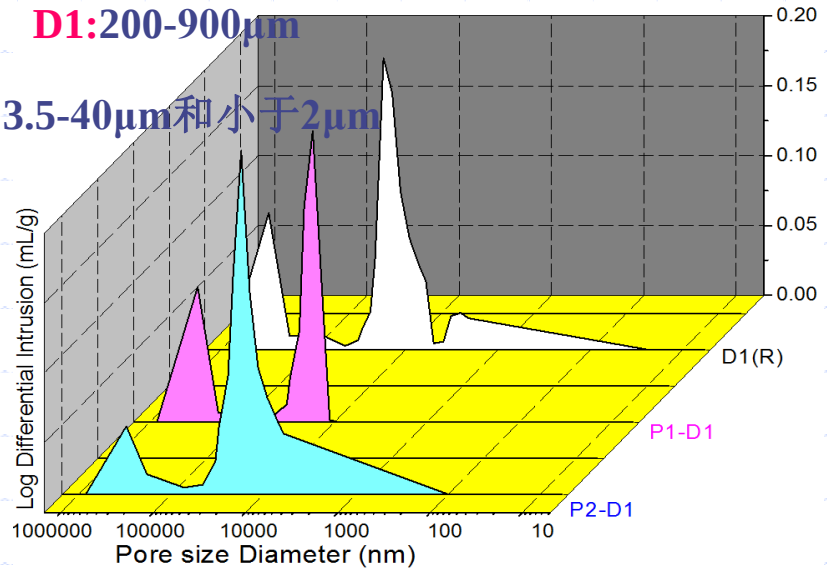
P1——*ap*-POSS-PMMA$_{152}$-b-P(MA-POSS)$_{8.4}$

P2——PDMS-b-PMMA$_{408}$-b-P(MA-POSS)$_{8.2}$



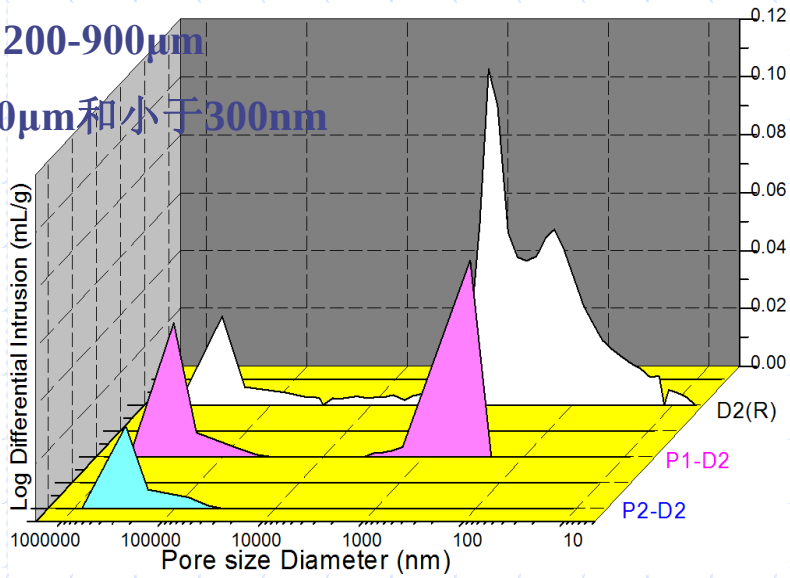
D1:200-900μm

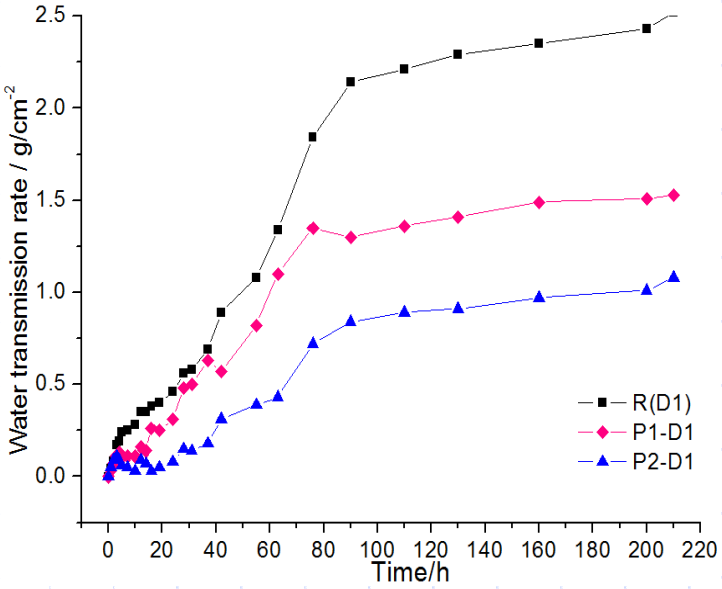
3.5-40μm和小于2μm

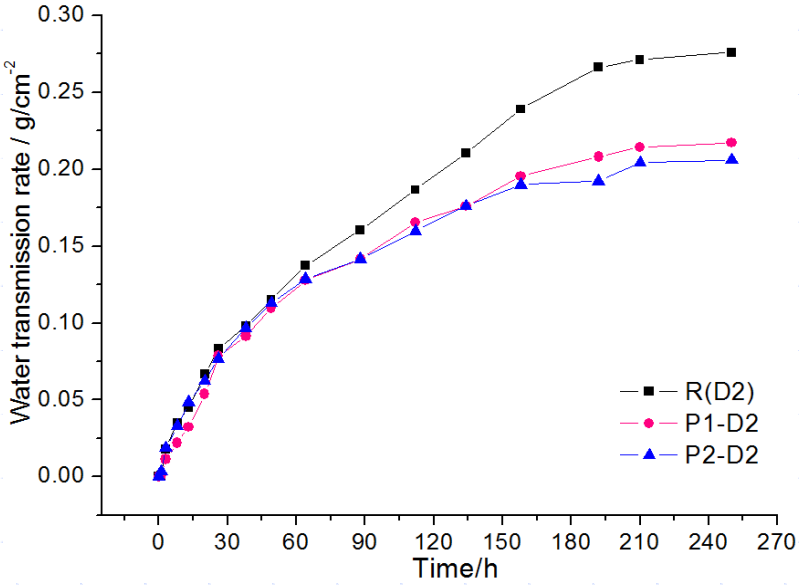


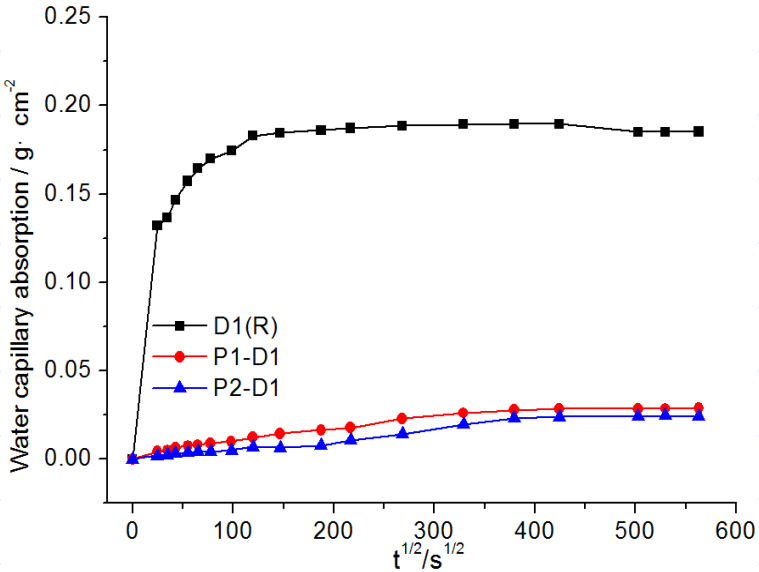
D2:200-900μm

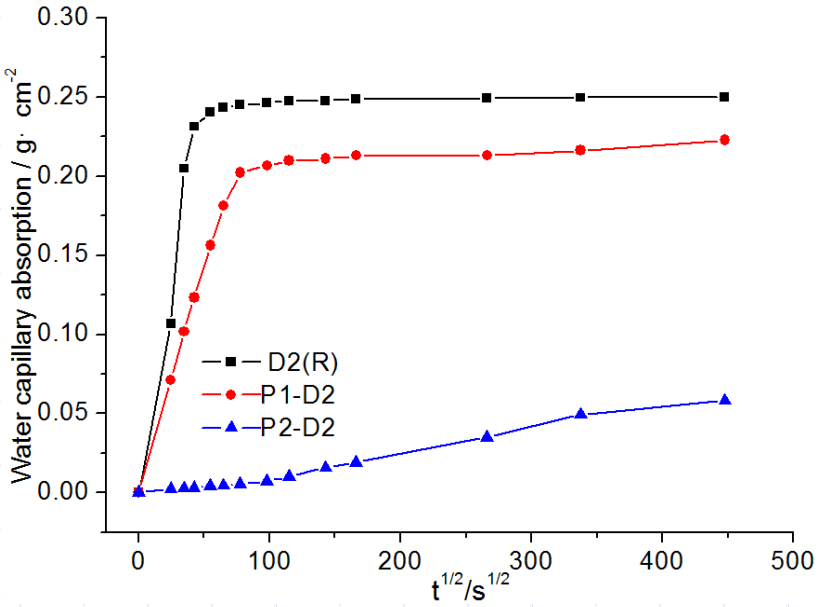
0.3-20μm和小于300nm




Water transmission rate / g/cm-2
Time/h
R(D1)
P1-D1
P2-D1

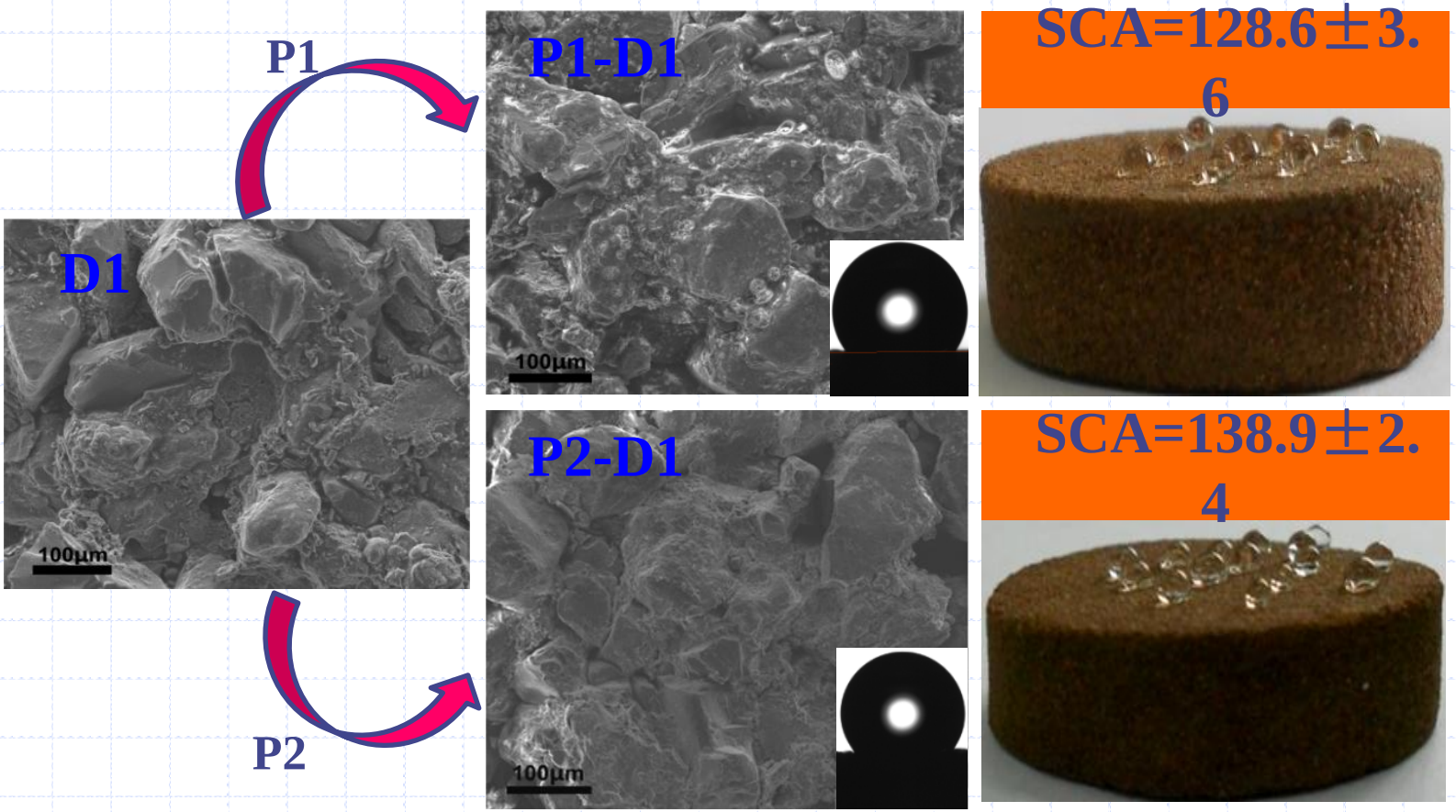

Water transmission rate / g/cm-2
Time/h
R(D2)
P1-D2
P2-D2


Water capillary absorption / g· cm-2
t1/2/s1/2
D1(R)
P1-D1
P2-D1


Water capillary absorption / g· cm-2
t1/2/s1/2
D2(R)
P1-D2
P2-D2

Materials	CA/g·cm^{-2}·s$^{-1/2}$	Water absorption/wt%
R(D1)	1.53×10^{-3}	6.89
P1-D1	7.89×10^{-5}	2.46
P2-D1	**6.58×10^{-5}**	**2.22**
R(D2)	2.50×10^{-3}	11.15
P1-D2	1.98×10^{-3}	8.42
P2-D2	**1.47×10^{-4}**	**5.95**

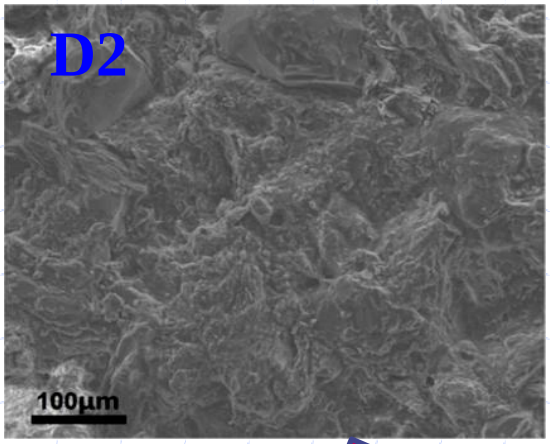
ap-POSS-PMMA$_{152}$-b-P(MA-POSS)$_{8.4}$



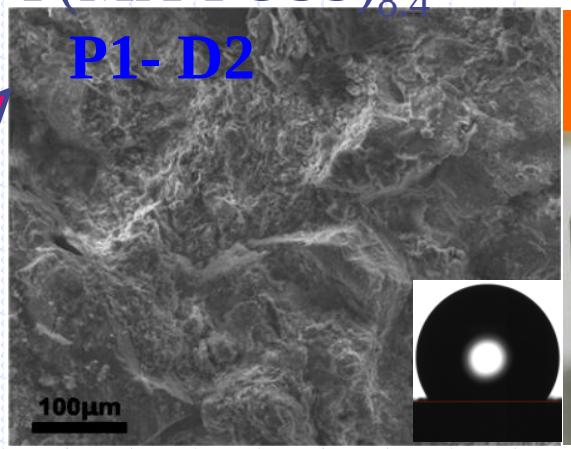
PDMS-b-PMMA$_{408}$-b-P(MA-POSS)$_{8.2}$

ap-POSS-PMMA$_{152}$-b-P(MA-POSS)$_{8.4}$

P1

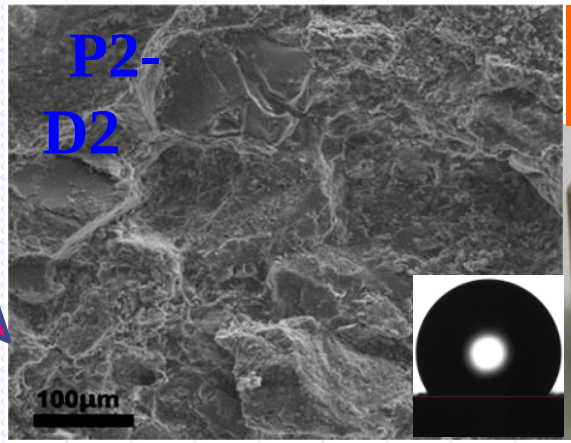


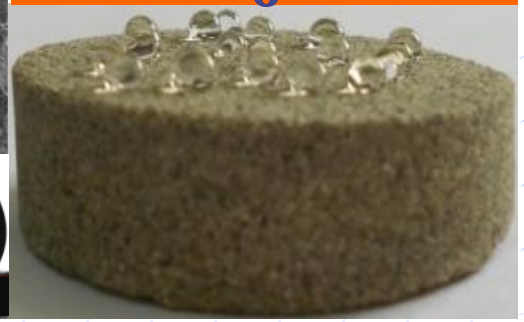
P2





SCA=122.9±2.1



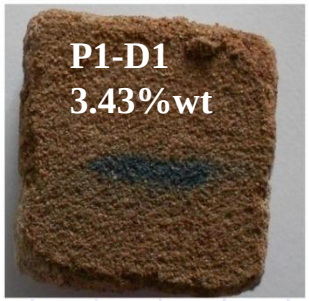


SCA=128.7±1.6

PDMS-b-PMMA$_{408}$-b-P(MA-POSS)$_{8.2}$

D1-







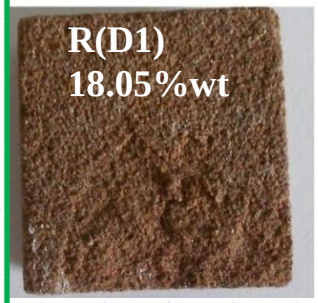
D2-

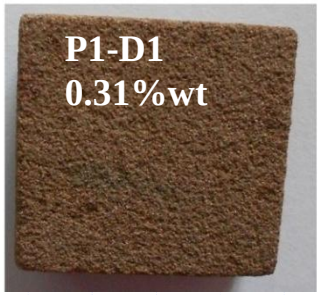


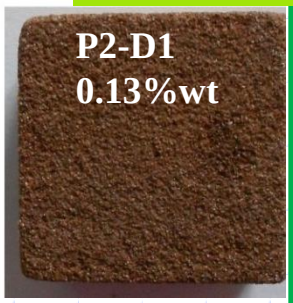


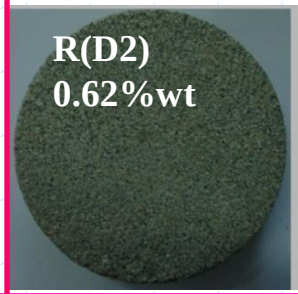


9cycles for salt-crystallization

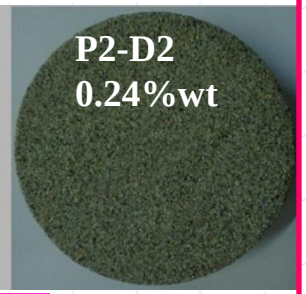






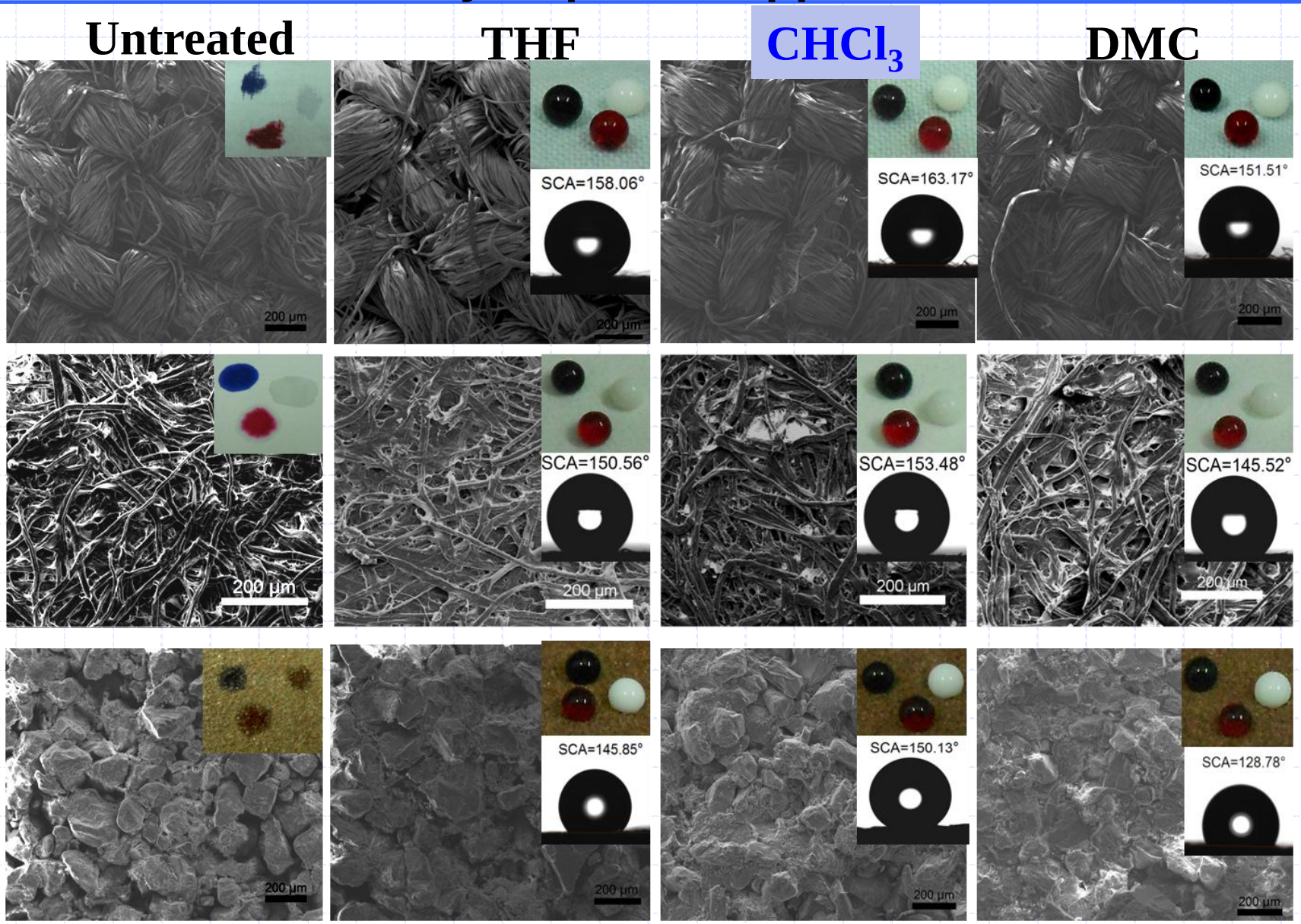




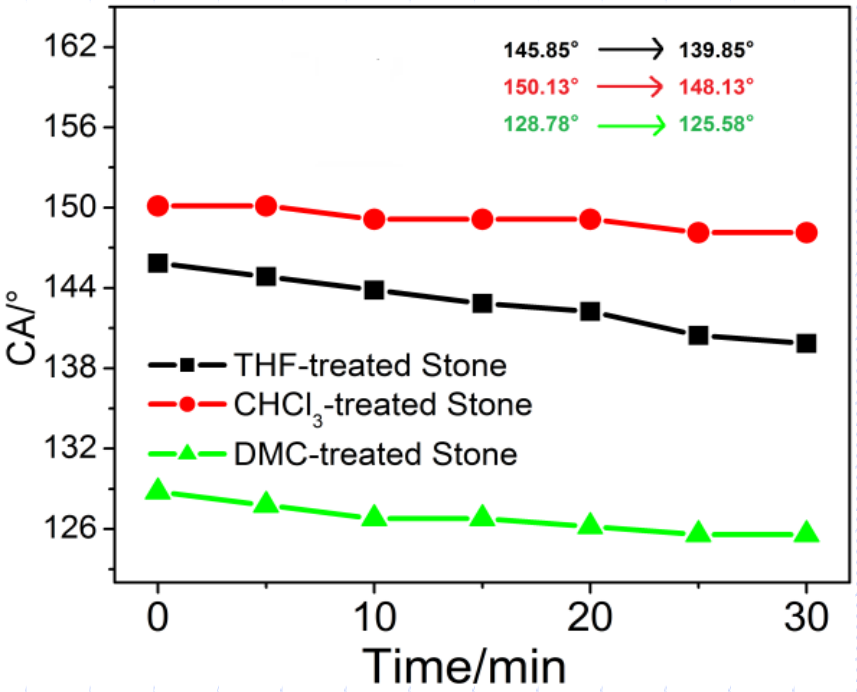


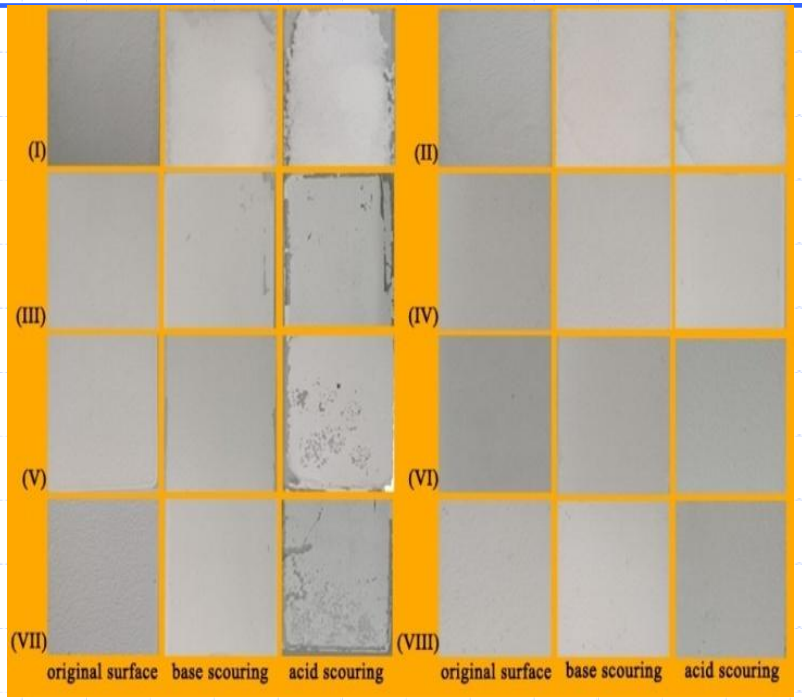
60 cycles for freeze-throwing

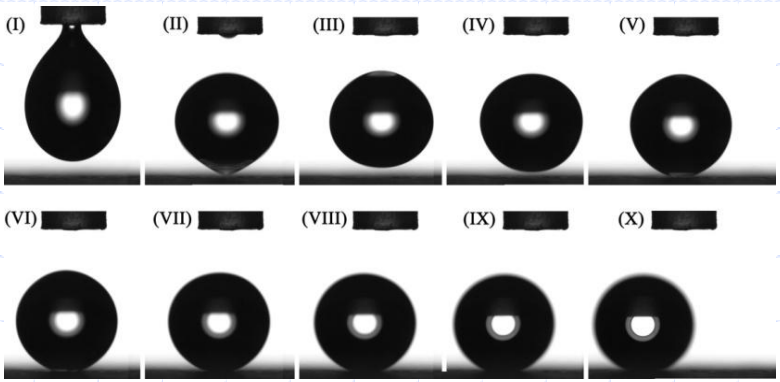
3.2 Hydrophobic application

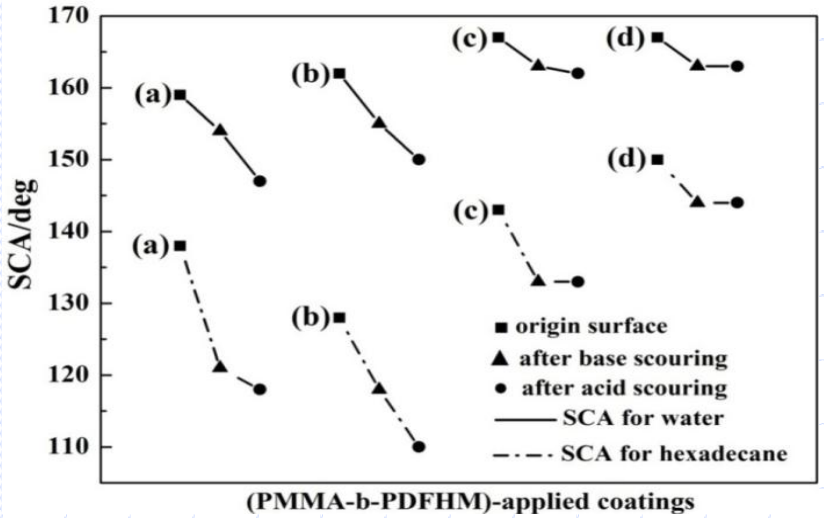


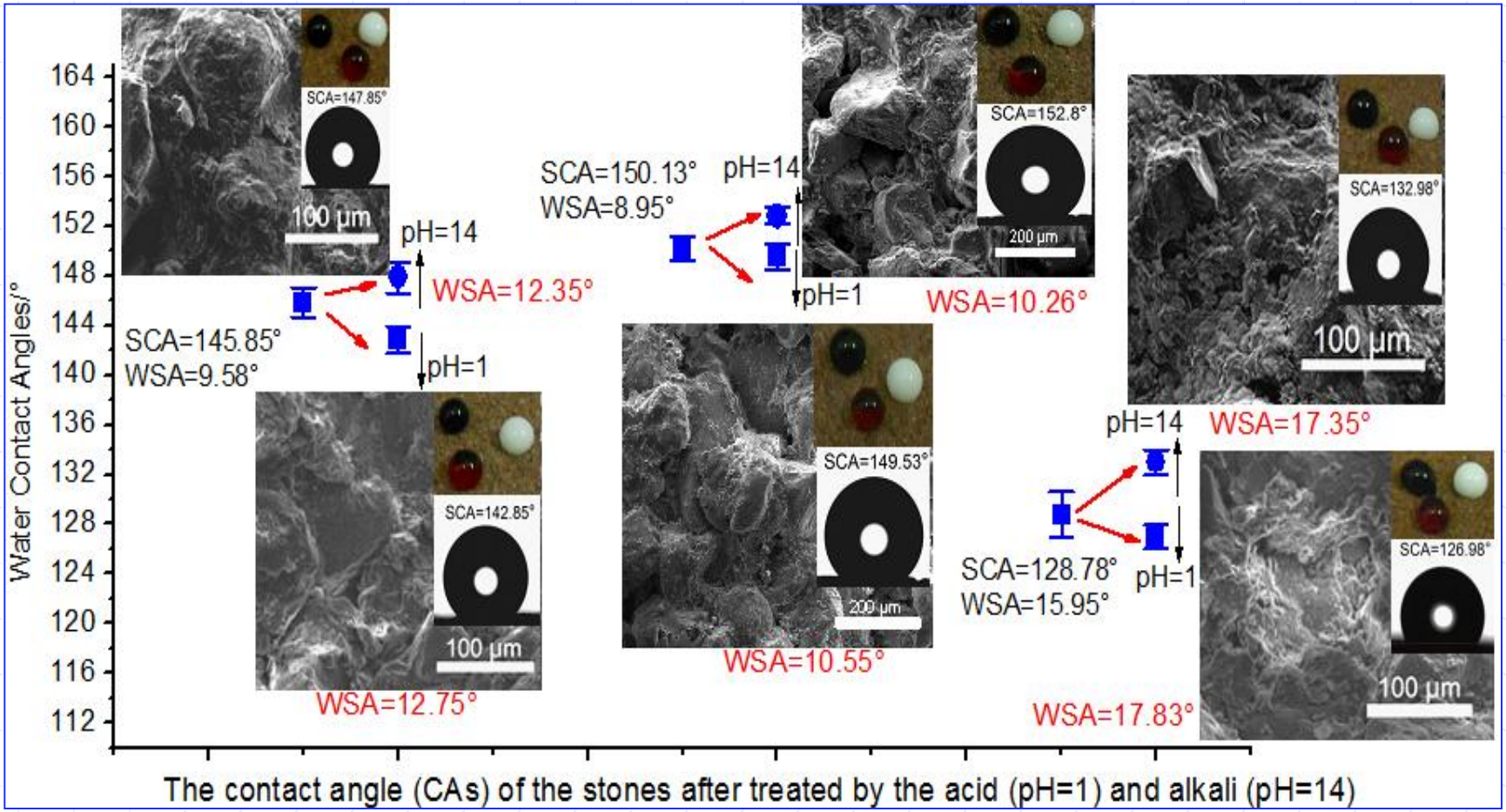
ap-POSS-PMMA-b-PDFHM


145.85° → 139.85°
150.13° → 148.13°
128.78° → 125.58°
CA/°
Time/min
THF-treated Stone
CHCl3-treated Stone
DMC-treated Stone


(I)
(II)
(III)
(IV)
(V)
(VI)
(VII)
(VIII)
original surface
base scouring
acid scouring


(I)
(II)
(III)
(IV)
(V)
(VI)
(VII)
(VIII)
(IX)
(X)


SCA/deg
(a)
(b)
(c)
(d)
origin surface
after base scouring
after acid scouring
SCA for water
SCA for hexadecane
(PMMA-b-PDFHM)-applied coatings


Water Contact Angles/°
164
160
156
152
148
144
140
136
132
128
124
120
116
112
SCA=147.85°
100 μm
pH=14
WSA=12.35°
SCA=145.85°
WSA=9.58°
pH=1
SCA=142.85°
100 μm
WSA=12.75°
SCA=150.13°
WSA=8.95°
pH=14
pH=1
SCA=152.8°
200 μm
WSA=10.26°
SCA=149.53°
200 μm
WSA=10.55°
SCA=132.98°
100 μm
pH=14
WSA=17.35°
SCA=128.78°
WSA=15.95°
pH=1
SCA=126.98°
100 μm
WSA=17.83°
The contact angle (CAs) of the stones after treated by the acid (pH=1) and alkali (pH=14)

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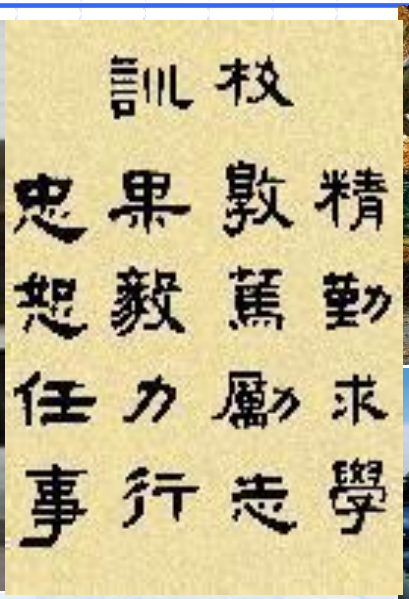
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National Science Foundation of China (NSFC)

No. 51373133, 51073126

No. 51373133, No.51210305018


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忠果敦精
想毅篤勤
任力勵求
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Thank you all for your attention!