Synthesis and Characterizations of Poly(oxyethylene) Derivatives and Polysiloxane Derivatives for Extreme-UV Lithography

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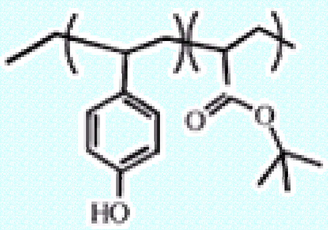
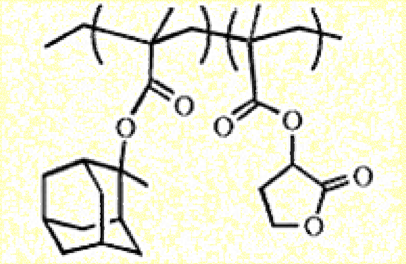
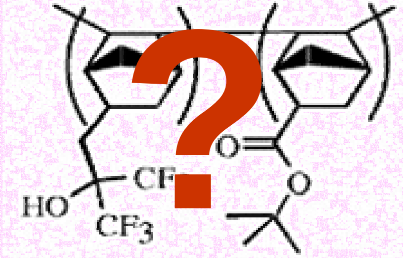
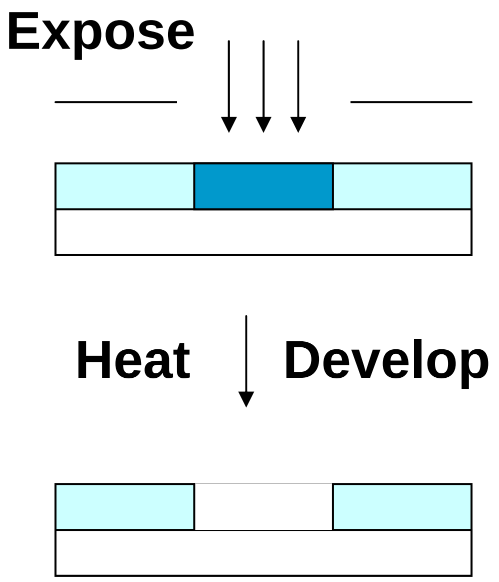
Introduction : Typical Chemically Amplified Photoresist

KrF(248nm)	ArF(193nm)	F_2(157nm)	EUV(13.4nm)
			C, H, O, B & Si

Node Definition	**180nm**	🟩	**130nm**	🟩	**100nm**	🟩	**70nm**	🟩	**50nm**	🟩

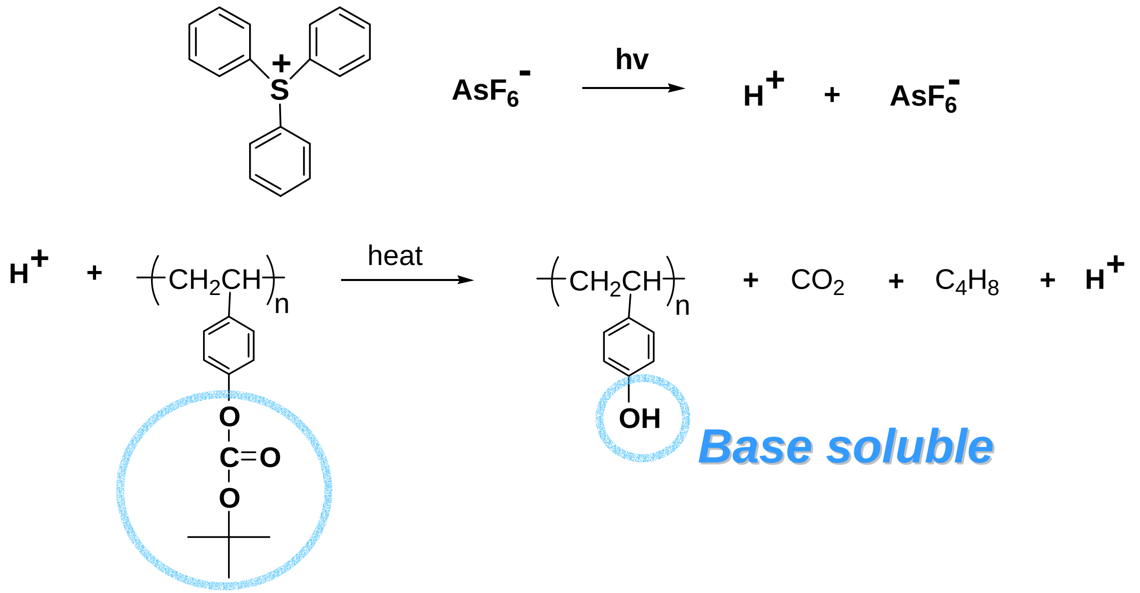
❖ Mechanism



Expose

Heat

Develop

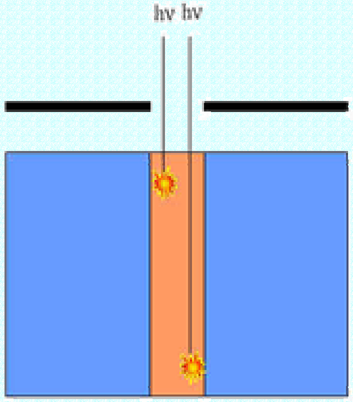


Base soluble

Introduction : Requirements for EUVL Resist

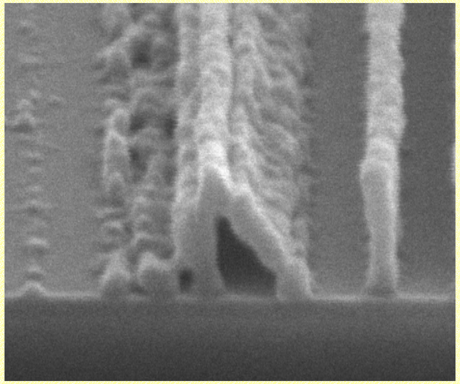
Lithographic parameter	Molecular characteristic
Absorption	Transparent at Extreme-UV
Substrate adhesion	Incorporation of polar moiety
Aqueous base solubility	OH, COOH, NH, etc
Aspect ratio	Surface tension and mechanical strength

Transparency

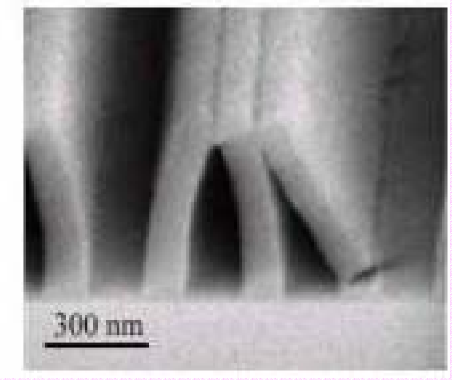


O.D. <1.0/㎛

Adhesion

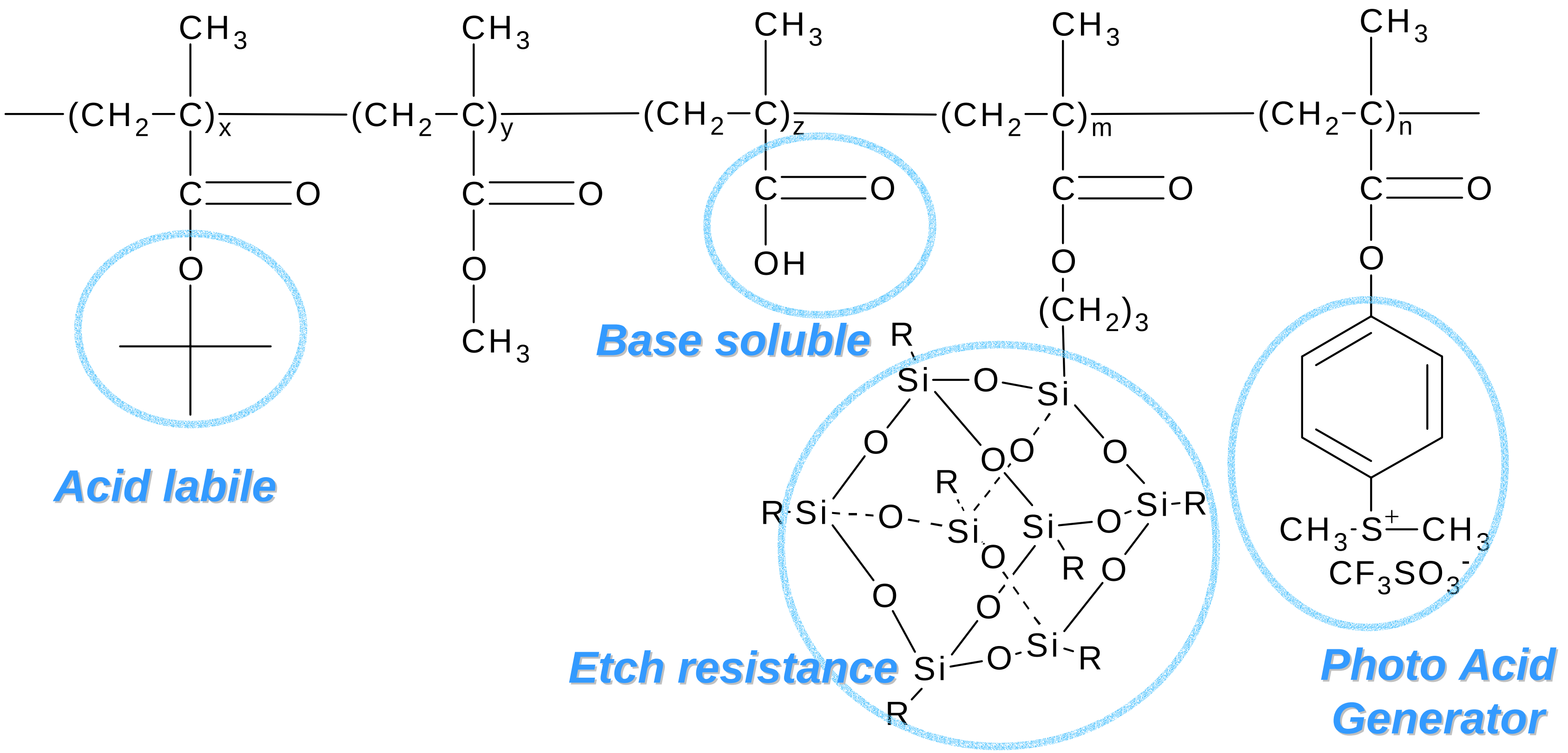


Aspect ratio



Sub.100nm <2.5

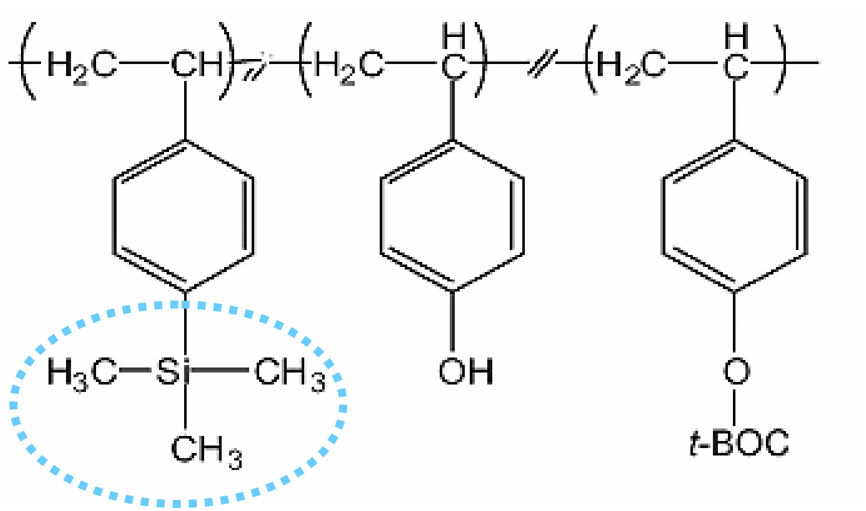
Introduction : Recent researches for EUVL Resist (1)



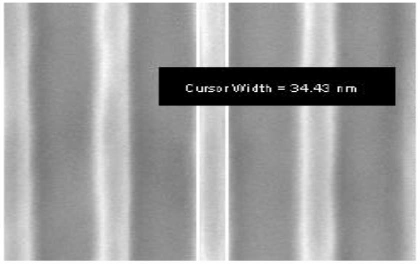
K. E. Gonsalves, Adv, Mater. 13, 19 5, 2001

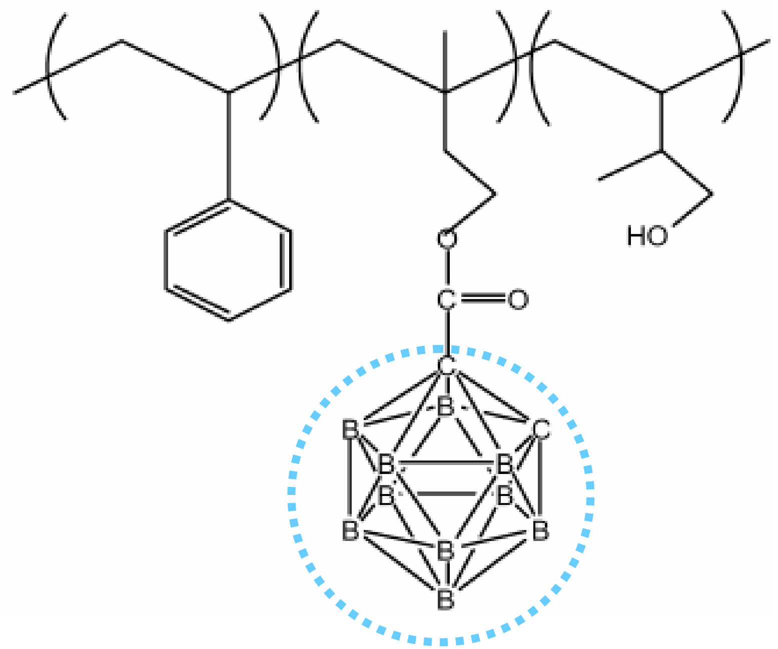
K. E. Gonsalves, Microelectron. Eng. 65, 454, 2003

Introduction : Recent researches for EUVL Resist (2)



Node : 22.5nm





The lack of stability towards air and moisture!

C. K. Ober, Proc. SPIE (2003)

- ✓ **Silicon** and **Boron** is highly Extreme-UV transparent element & enhanced the oxygen etch resistance.

Objectives

❖ Synthesis of Monomer

- introduction of acid labile group
- functional group for base solubility
- functional group for etch resistance

❖ Polymerizations

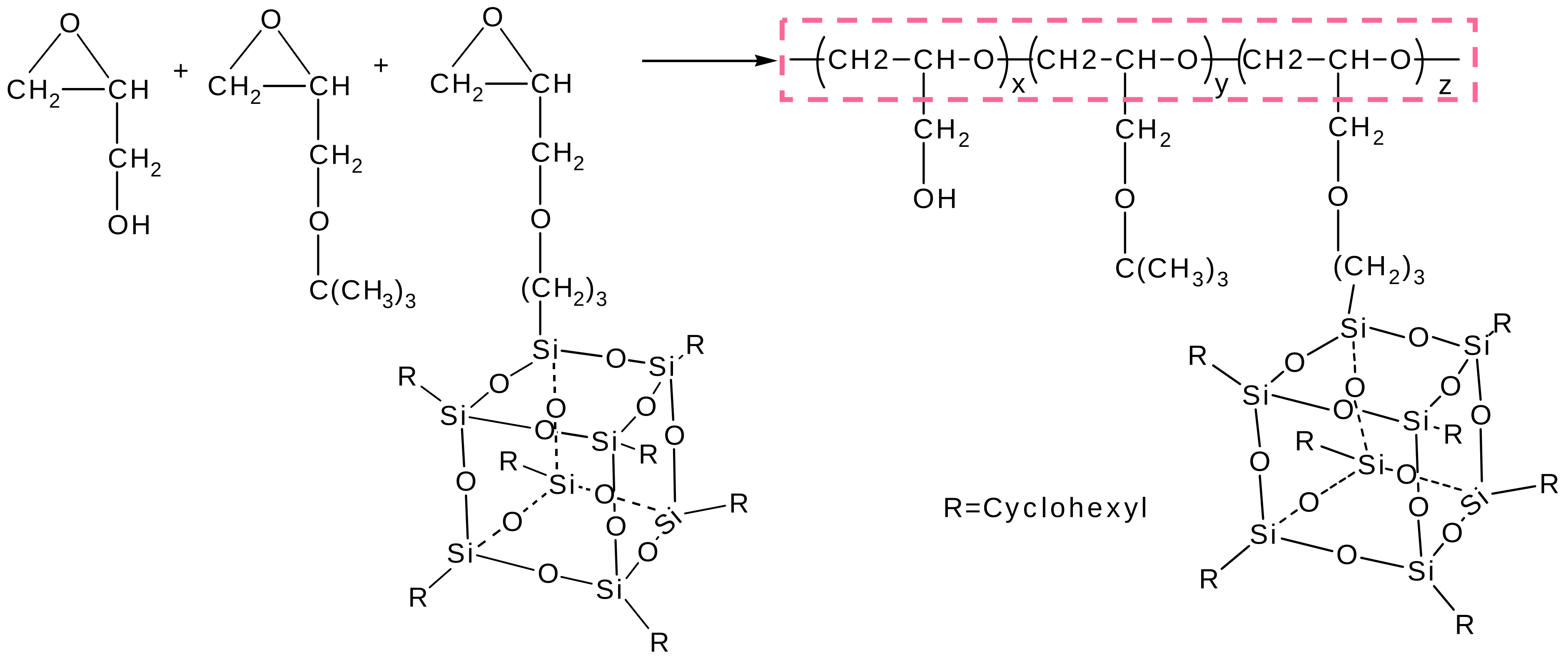
- optimized polymerization condition
- control of molecular weight
- polymers with high adhesion & strength

❖ Characterizaitons

- structural analysis
- adhesion
- surface uniformity

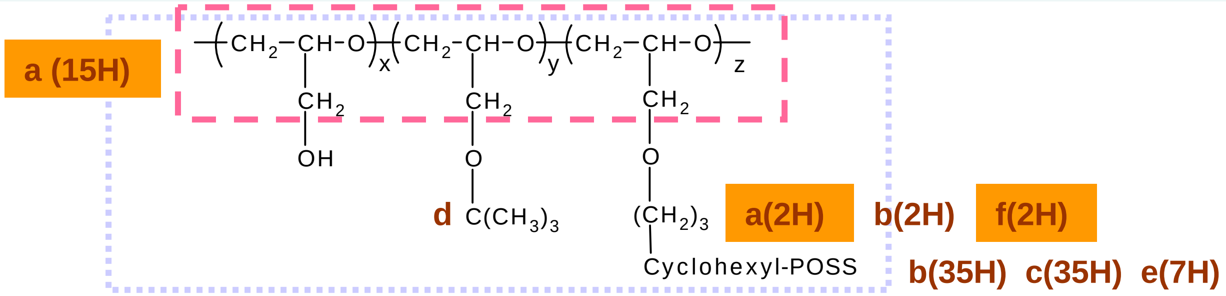
Target Polymer (1): Poly(oxyethylene) derivatives

Terpolymer

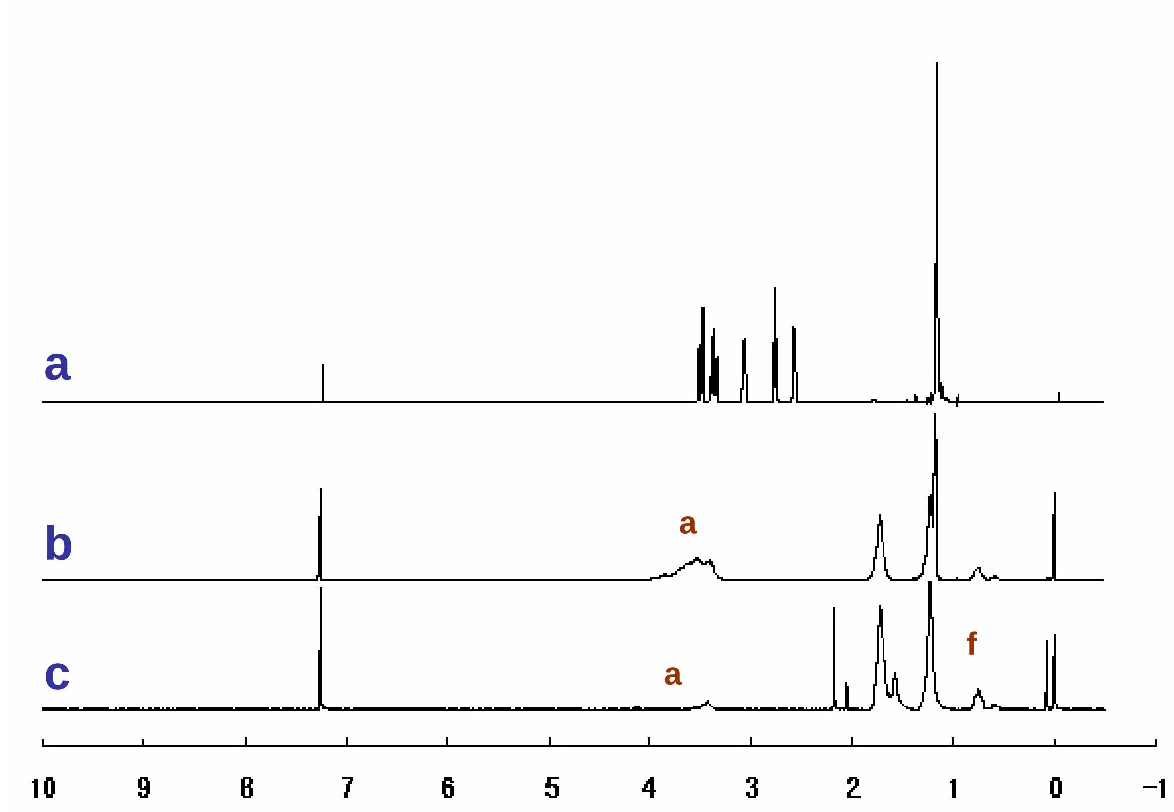


- ✓ Poly(oxyethylene) derivatives consisted of mostly low absorbing elements to 13.4 nm radiation including H, C, O and Si.
- ✓ Poly(oxyethylene)s gave good adhesion & surface uniformity due to the flexibility and functional groups.

Target Polymer (1): Structure analysis - NMR



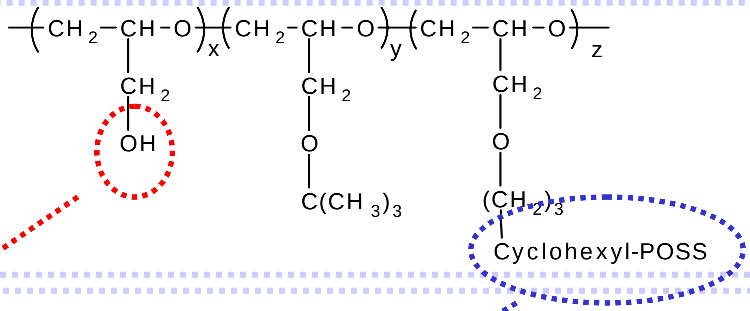
^{1}H NMR



- **(a) t-butylglycidyl ether (monomer)**
- **(b) Glycidyl-POSS homopolymer**
- **(c) Target polymer**

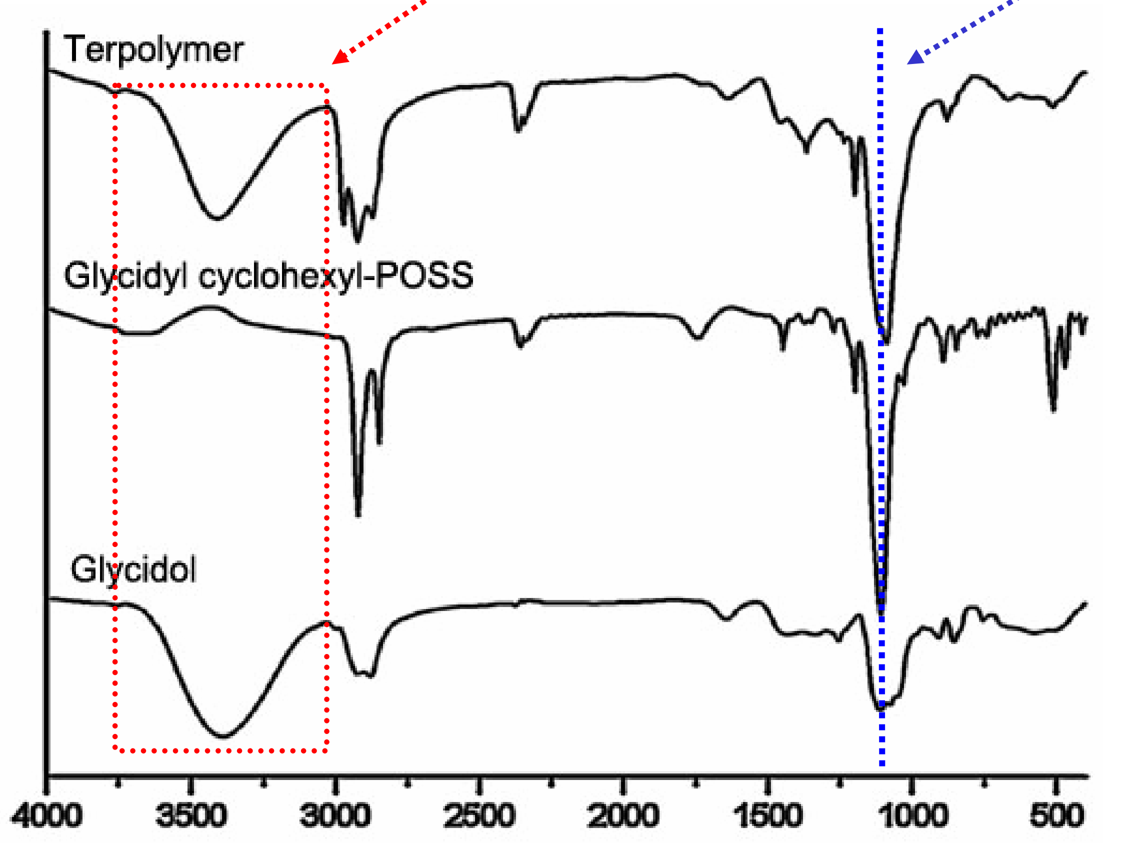
Peak Position	Chemical shift(ppm)
a	3.32-3.95(17H)
b	1.62-1.83(37H)
c	1.23-1.34(35H)
d	1.05-1.23(9H)
e	0.68-0.82(7H)
f	0.54-0.67(2H)

Target Polymer (1): Structure analysis - IR



$$-\!\left(CH_2-\underset{\underset{OH}{|}}{\underset{CH_2}{\underset{|}{CH}}}-O\right)_x\!\left(CH_2-\underset{\underset{C(CH_3)_3}{|}}{\underset{O}{\underset{|}{\underset{CH_2}{\underset{|}{CH}}}}}-O\right)_y\!\left(CH_2-\underset{\underset{\text{Cyclohexyl-POSS}}{|}}{\underset{(CH_2)_3}{\underset{|}{\underset{O}{\underset{|}{\underset{CH_2}{\underset{|}{CH}}}}}}}-O\right)_z\!-$$

FT-IR



Type of group	Region (cm^{-1})
-OH	3100-3700
O-Si-O	990-1100
C-H a/symmetric	2830-3010

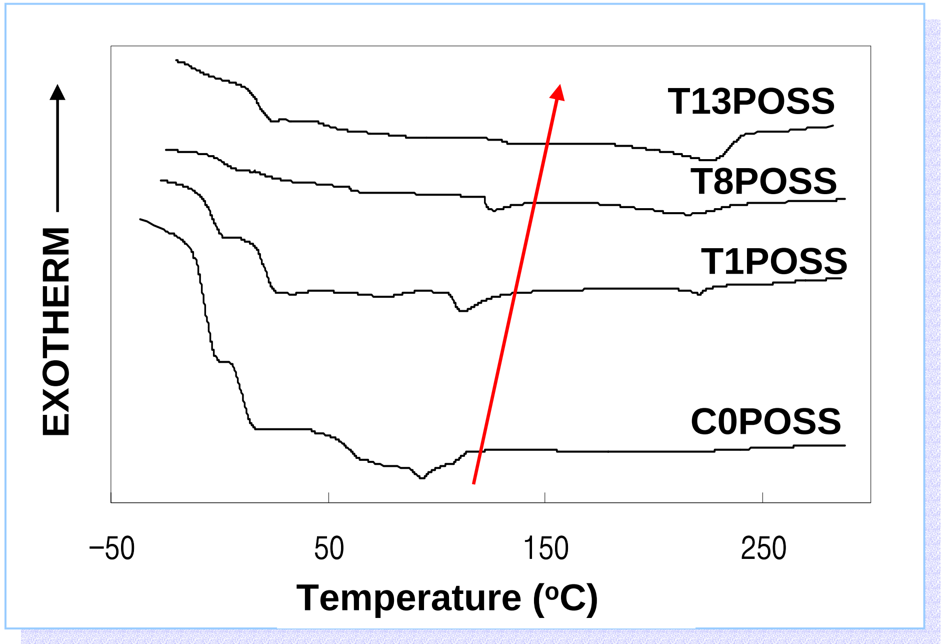
Target Polymer (1) : Reaction Condition

Terpolymer

	Compositions, loading (in polymer) [mol%]			Mn * 10^3 [g/mol]	PDI
	Glycidyl Cyclohexyl-POSS	Glycidol (-OH)	TBGE (-^{t}-Bu)		
C0POSS	0	45	55	4.73	2.41
T1POSS	1 (1.5)	57	42	3.03	1.66
T8POSS	5 (8.2)	40	55	3.98	2.00
T13POSS	10 (13.1)	40	50	3.85	2.28
H100POSS	100	0	0	2.81	1.43

- **Intiator concentration : 1mol% $BF_3 \bullet OEt_2$ of total monomers (= 63.4 µL)**
- **Reaction Temperature & Time : 0℃, 3days**
- **Gel permeation chromatography (GPC) analysis was carried out using THF as eluent and polystyrene as standard at 30℃.**

DSC Results of Terpolymers



Polymer	T_g (°C)	T_m (°C, (ΔH (J/g))
C0POSS	- 8.3 10.4	90.9 (4.7)
T1POSS	- 3.5 18.5	110.3 (1.7) 208.7 (0.2)
T8POSS	2.2 27.9	125.2 (0.9) 210.4 (2.6)
T13POSS	4.4 31.3	217.3 (5.8)

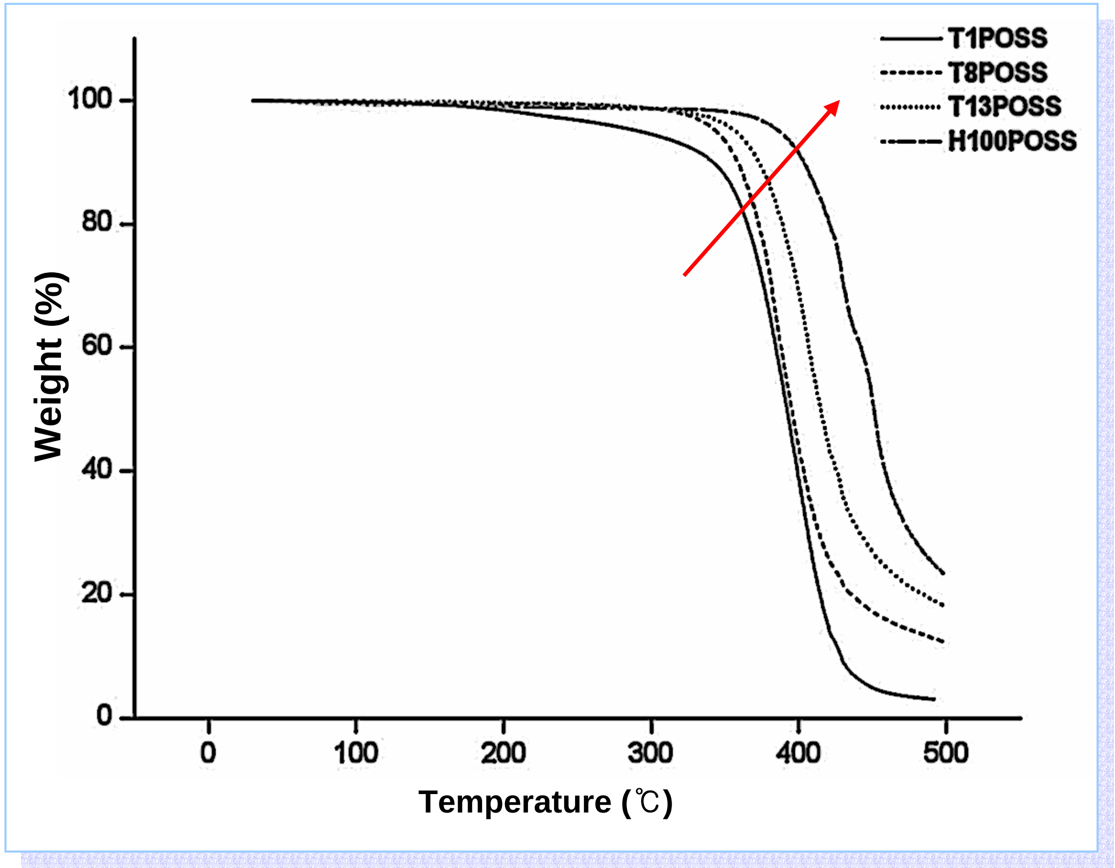
Increase

✓ DSC results show that the polymers have blocks (block copolymer).

✓ Upon incorporation of POSS, the increase of the T_g was observed.
(∵ the presence of POSS hinder the motion of the backbone.)

✓ Upon incorporation of POSS, the increase of the $T_{m,2}$ and the increase of ΔH were observed. (∵ ΔH data revealed that degree of crystallinity increased with incorporation of POSS)

TGA Results of Terpolymers

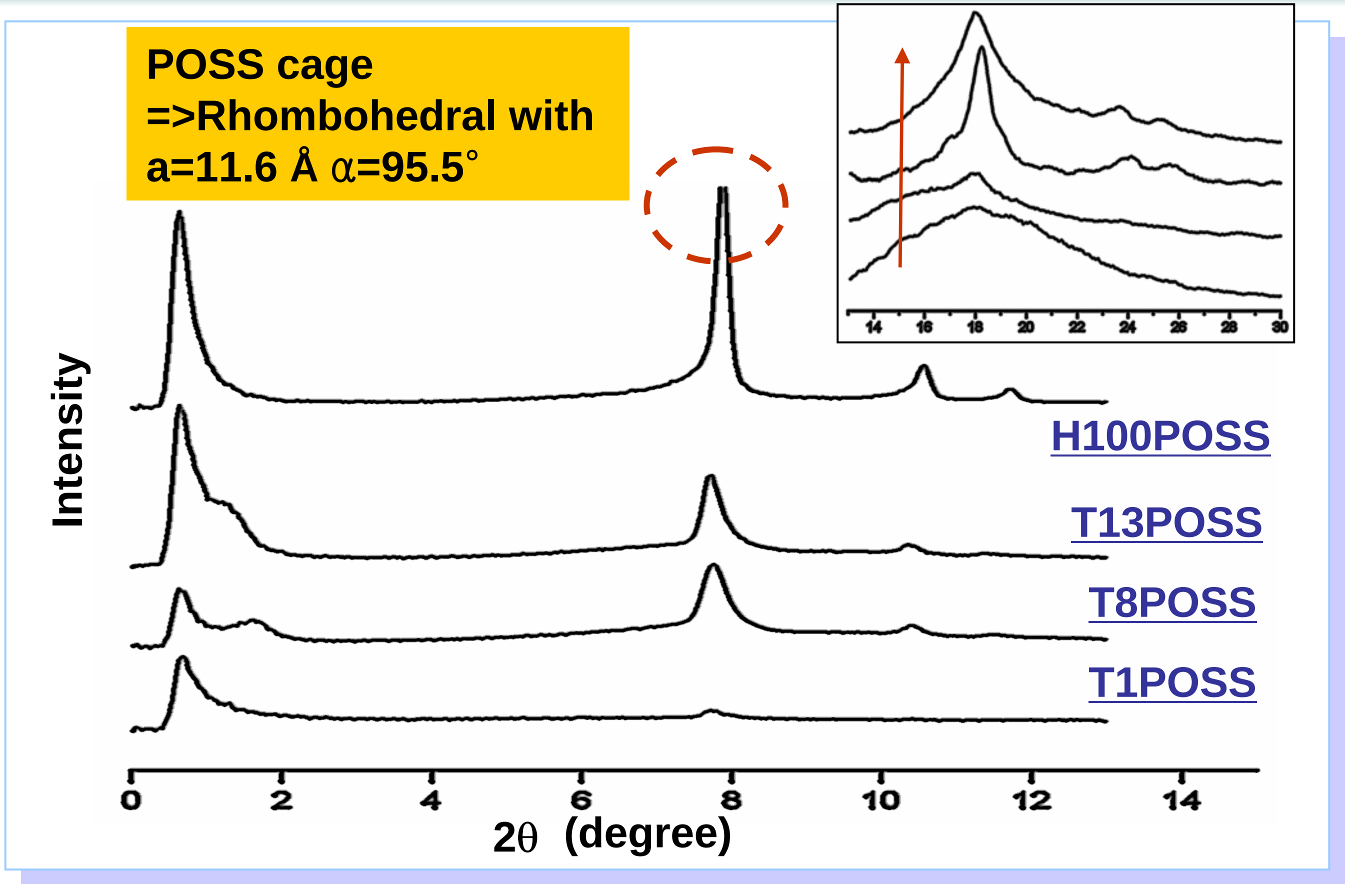


Polymer	$T_{d.\,0}$ (°C)	$T_{d,1/2}$ (°C)
T1POSS	341.9	391.7
T8POSS	358.3	395.5
T13POSS	373.3	415.6
H100POSS	403.5	450.9

Increase

✓ The polymer decomposition point was higher for those polymers with larger POSS content.

Powder X-ray Patterns of Terpolymers

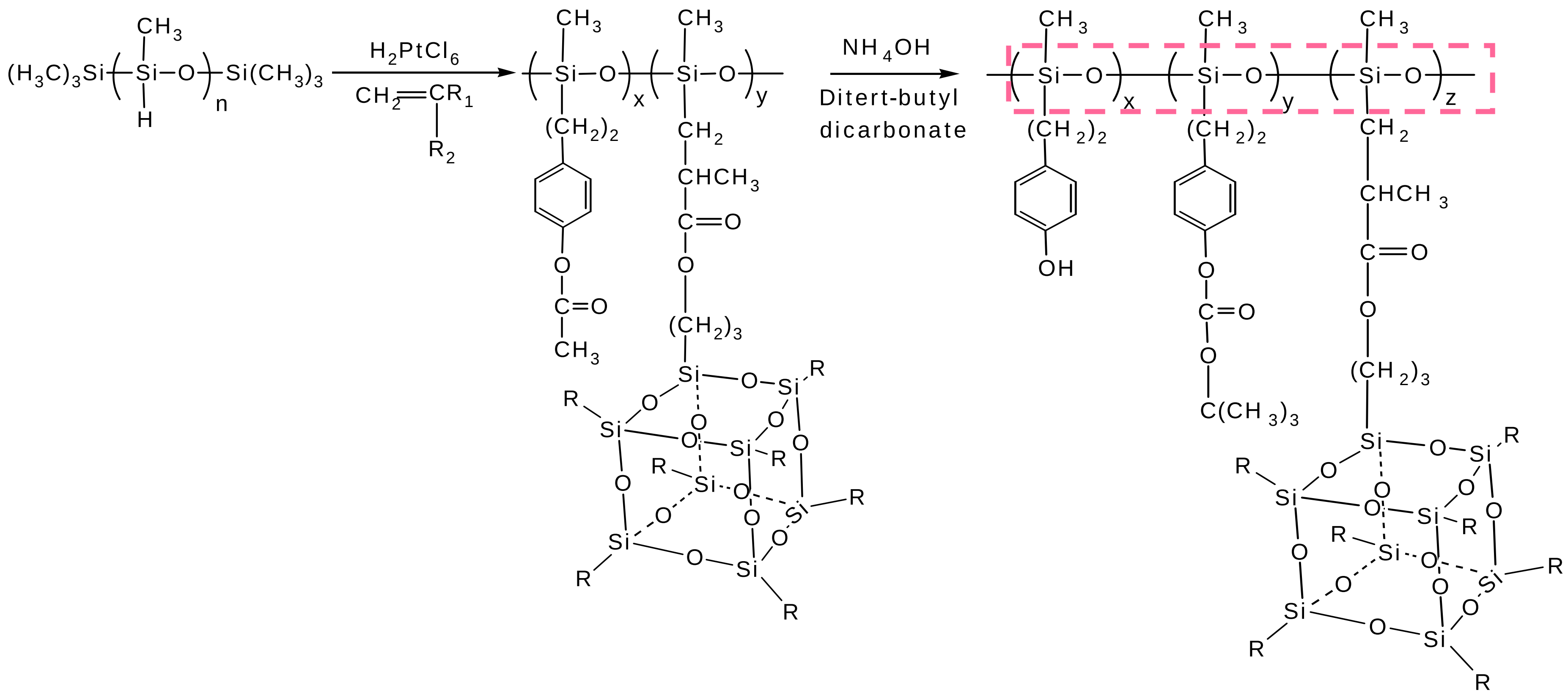


POSS cage
=>Rhombohedral with
a=11.6 Å α=95.5°

- ✓ Diffractograms of terpolymers showed charcteristic cyclohexyl-POSS crystalline peaks at d-spacing equal to 11.6, 8.4, 7.6, 4.9, 3.8, 3.5 Å.
- ✓ Upon increasing POSS contents in terpolymer, more intense and sharp peak as obtained.

Target Polymer (2) : Poly(methylhydrosiloxane) derivatives

Modified Poly(methylhydrosiloxane)



- ✓ Poly(methylhydrosiloxane)s consisted of mostly low absorbing elements to 13.4nm radiation including H, C, O and Si.
- ✓ Poly(methylhydrosiloxane)s gave good adhesion surface uniformity due to the flexibility and functional groups.

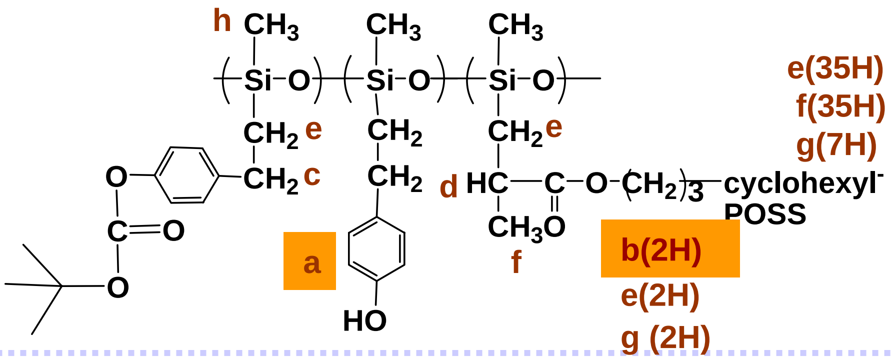
Target Polymer (2) : Reaction Condition

Nomenclature	Compositions, loading [mol%]			Mn * 10^3 [g/mol]	PDI
	MMA-POSS	*p*-acetoxystyrene	PHMS		
PMHS	0	0	100	2.90	4.24
M-PMHS3	1(3.1)	99	100	-	-
M-PMHS8	5(8.3)	95	100	-	-

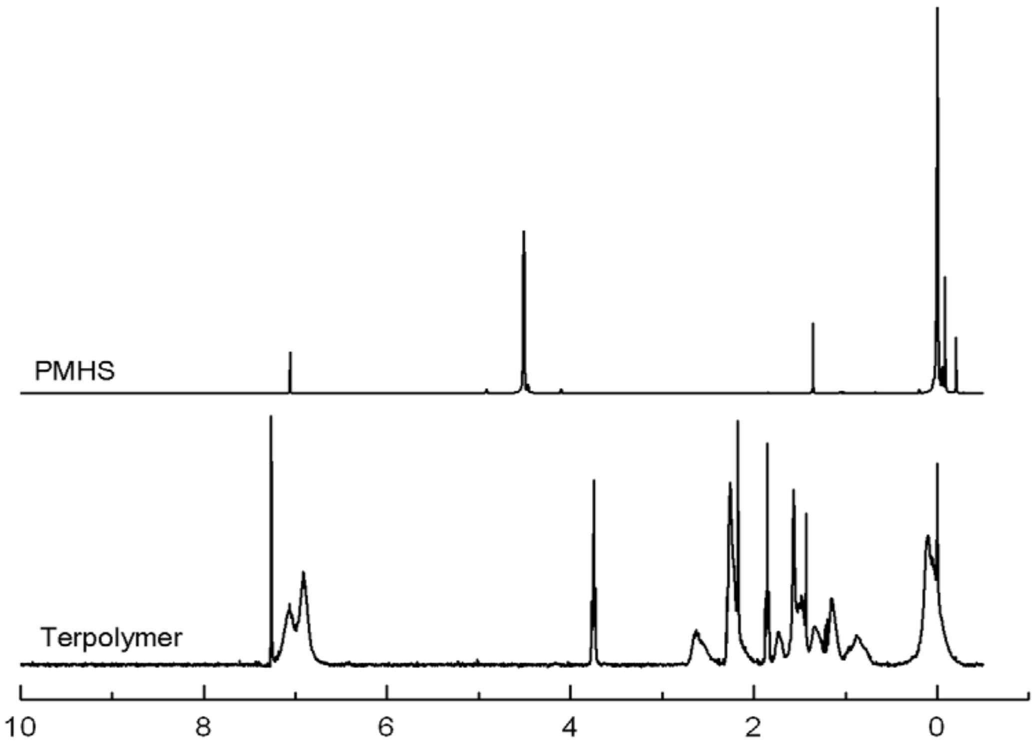
- **catalyst concentration : $H_2PtCl_6 \cdot 6H_2O$ / isopropyl alcohol 0.05g/mL (100 μL)**
- **Reaction Temperature & Time : RT for 1day and then 70℃ for 1day**

Nomenclature	Compositions (in polymer) [mol%]			Mn * 10^3 [g/mol]	PDI
	MMA-POSS	-OH	t-BOC		
M-PMHS3A	3	55	45	7.10	6.57
M-PMHS3B	3	45	55	7.21	8.90
M-PMHS8	8	45	55	7.87	4.70

Target Polymer (2) : Structure analysis - NMR

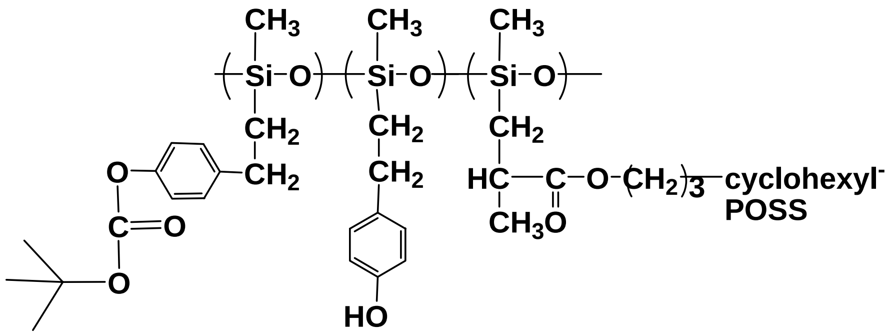


^{1}H NMR

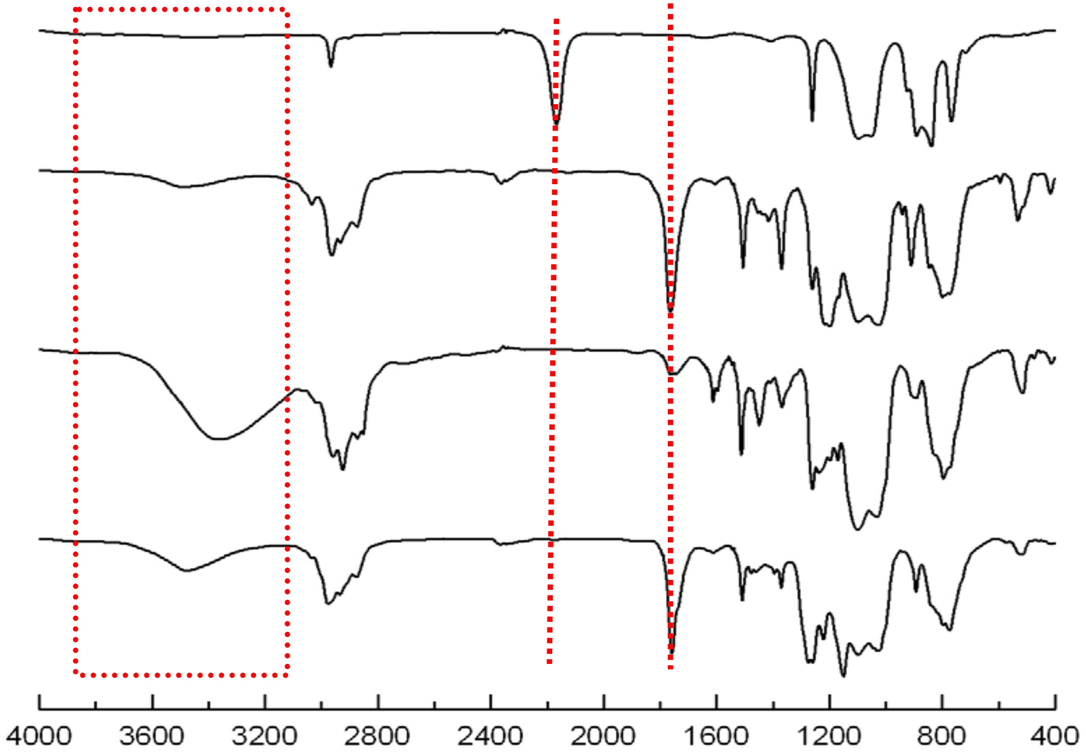


Peak Position	Chemical shift (ppm)
a	6.91-7.03 (4H)
b	3.72-3.77 (2H)
c	2.62-2.65 (2H)
d	2.25-2.31 (1H)
e	1.39-1.78 (41H)
f	1.15-1.38 (38H)
g	0.74-0.89 (9H)
h	0.10-0.23 (9H)
Si-H	4.7 (1H)

Target Polymer (2) : Structure analysis - IR

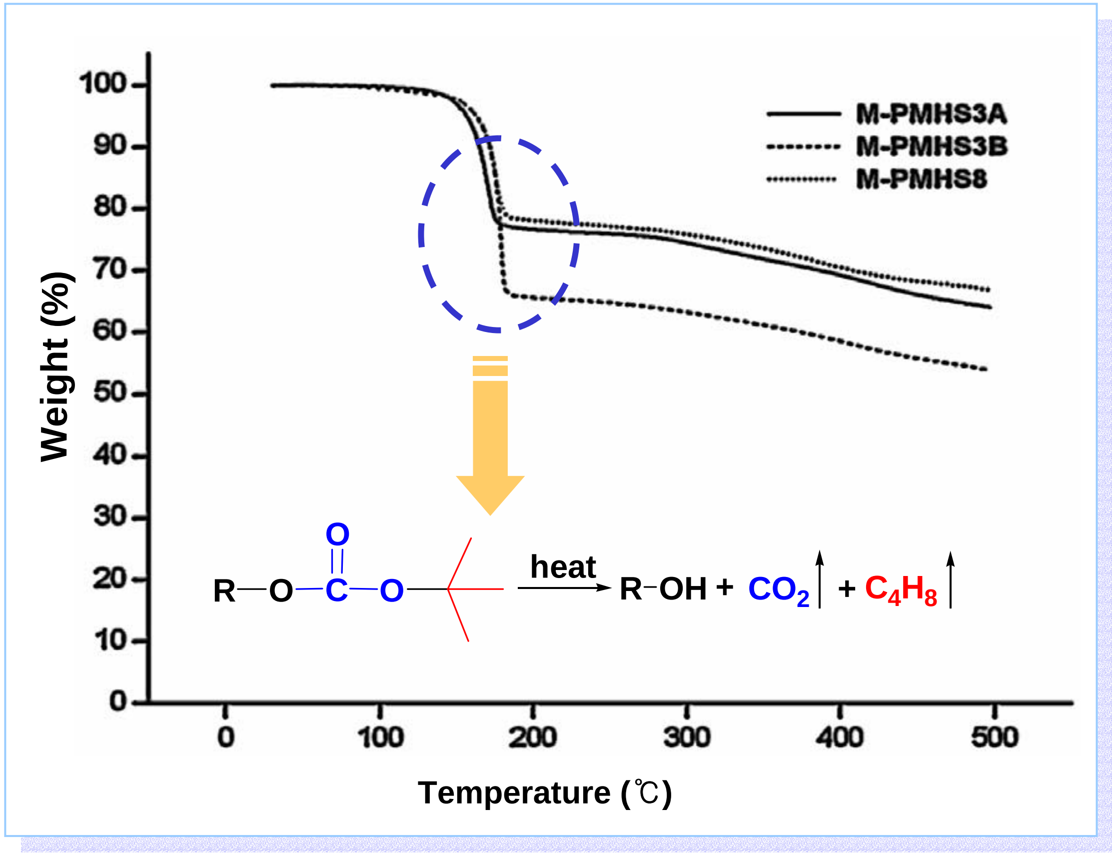


FT-IR



Type of group	Region (cm^{-1})
C-H a/symmetric	2830-3010
C=O	1700-1820 (s)
O-Si-O	1100-990 (vs)
O-H	3600-3000
Si-H	2250 (vs)

Thermal Stability of Target Polymer (2)



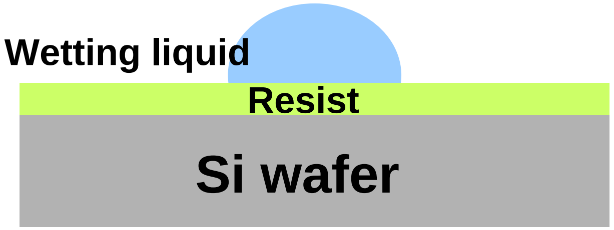
Polymer	$T_{d,0}$ (°C)	$T_{d,1/2}$ (°C)
M-PMHS3A	165.4	>500
M-PMHS3B	172.1	>500
M-PMHS8	174.8	>500

Increase

- ✓ The *t*-BOC group cleaved carbon dioxide and isobutene at about 200 °C.
- ✓ The polymer decomposition point was higher for those polymers with larger POSS content.

Work of adhesion

❖ Sessile drop method



Reference	γ_L^{L}	γ_L^{SP}	γ_L (mJ/m^2)
Water	21.8	51.0	72.8
Diiodomethane	50.4	0.40	50.8
Si wafer	33.3	13.5	46.8

Young-Dupre equation :

$$\gamma_L(1+\cos\theta) = 2\sqrt{\gamma_L^{L}\cdot\gamma_S^{L}} + 2\sqrt{\gamma_L^{SP}\cdot\gamma_S^{SP}}$$

$$(\gamma_L = \gamma_L^{L} + \gamma_L^{SP})$$

Owens and Wendt’s equation :

$$\boxed{W_A} = 2\sqrt{(\gamma_{Si})^{L}\cdot(\gamma_S)^{L}} + 2\sqrt{(\gamma_{Si})^{SP}\cdot(\gamma_S)^{SP}}$$

Work of adhesion

Nomenclature	Contact angle (^{0})		W_{ps} (mJ/m^2)
	H_2O	CH_2I_2	
T1POSS	66.7	39.2	94.9
T8POSS	70.6	41.6	91.9
T13POSS	87.0	42.5	81.1
H100POSS	79.6	48.8	84.2
M-PMHS3	75.3	43.5	88.4
M-PMHS8	78.9	48.2	84.5
PVP-based resist(APEX-E)	54.8	73.5	70.36
HMDS-primed Si	61.9	58.3	-

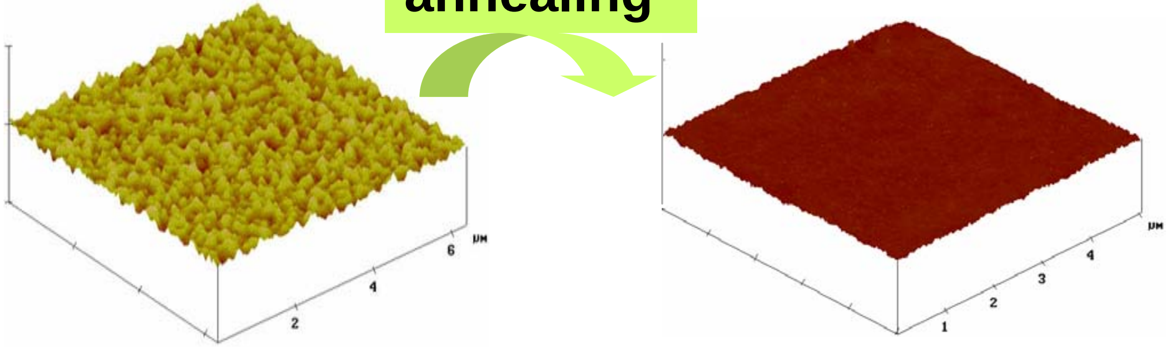
✓ The terpolymers revealed the much improved adhesion properties to silicon substrate in comparision with commercially available APEX-E.

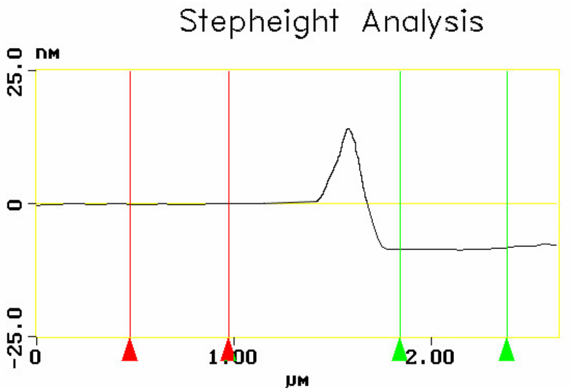
✓ Poly(oxyethylene) derivatives gave little more good adhesion than Poly(methylhydrosiloxane) derivatives.

Surface uniformity

T8POSS

annealing





RMS(root-mean-square) : 2 nm

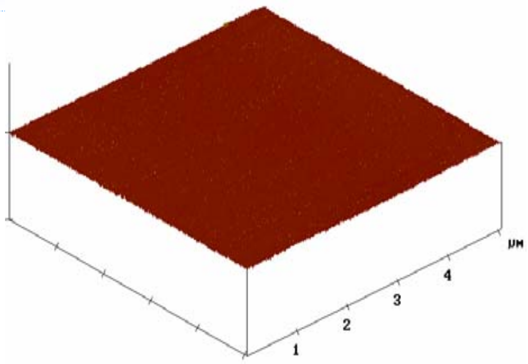
film thickness :17 nm

→

RMS(root-mean-square) : 0.5 nm

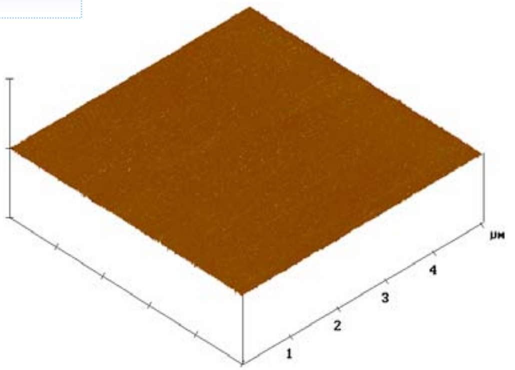
film thickness : 9 nm

M-PMHS3



RMS(root-mean-square) : 0.2 nm

M-PMHS8



RMS(root-mean-square) : 0.5 nm

✓ **A 6*6 μm^2 image revealed a smooth surface. (z : 20nm/div)**

Conclusions

- New photoresists were synthesized for extreme-UV lithography by ring-opening polymerization and hydrosilylation processes.

- Upon the incorporation of POSS, decomposition temperature and crystallinity of terpolymer were increased.

- PEO and PMHS backbone was found to increase the adhesion and surface uniformity of the polymers on the Si wafer due to the flexibility and functional groups.

Future Works

- Random copolymer will synthesize for appropriate photoresist by controlling monomer dropping time.
- The Extreme-UV lithographic evaluation of the polymers will be investigated under 13.4 nm exposure.
- Etch resistance and transparency of polyhedral oligosilses-quioxane(POSS) incorporated polymers will be investigated at Extreme-UV.