

# Design and Evaluation of Novel Fluoropolymer for 157nm Pellicle

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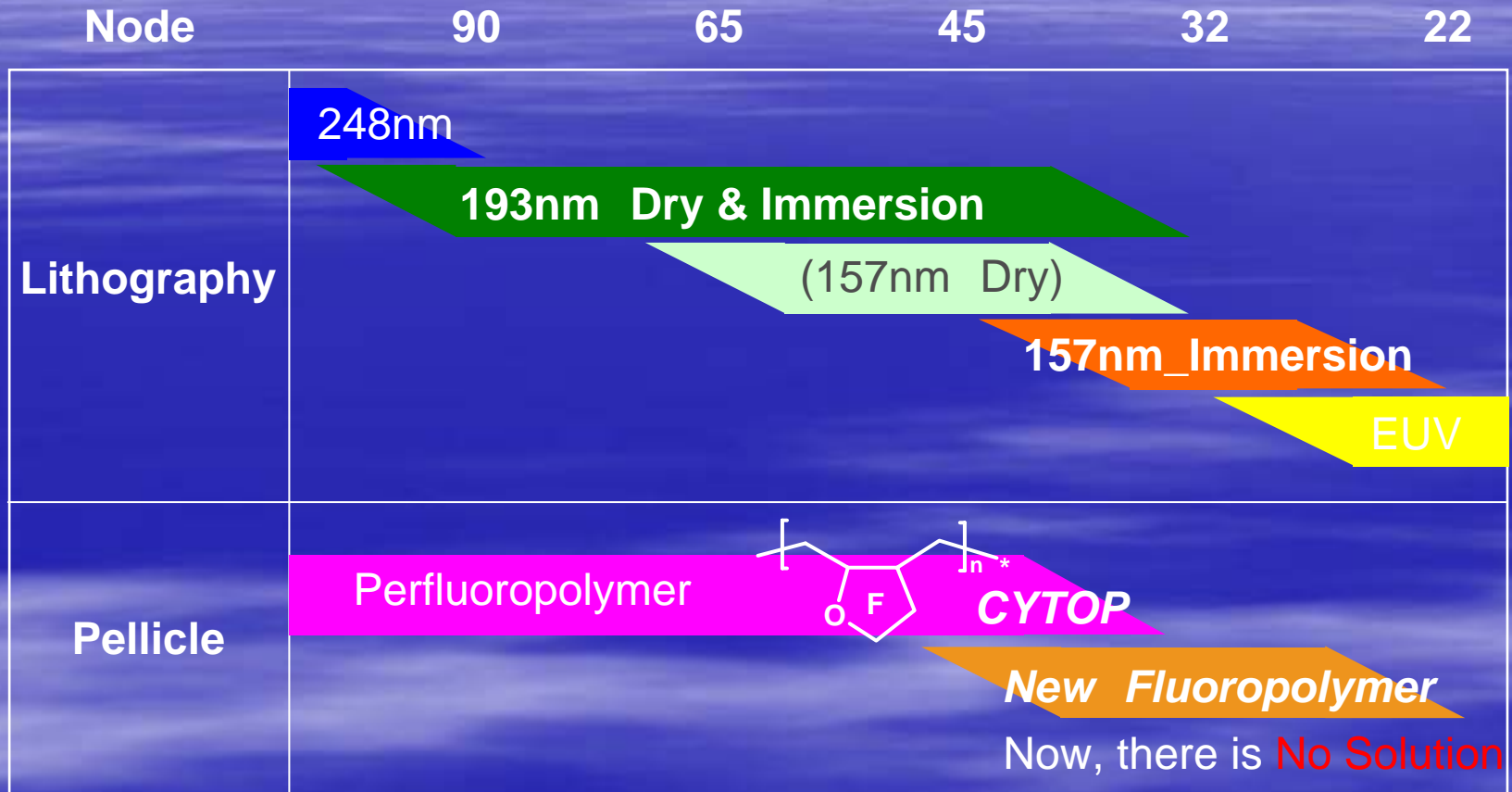
3 Aug. 2004

# Outline

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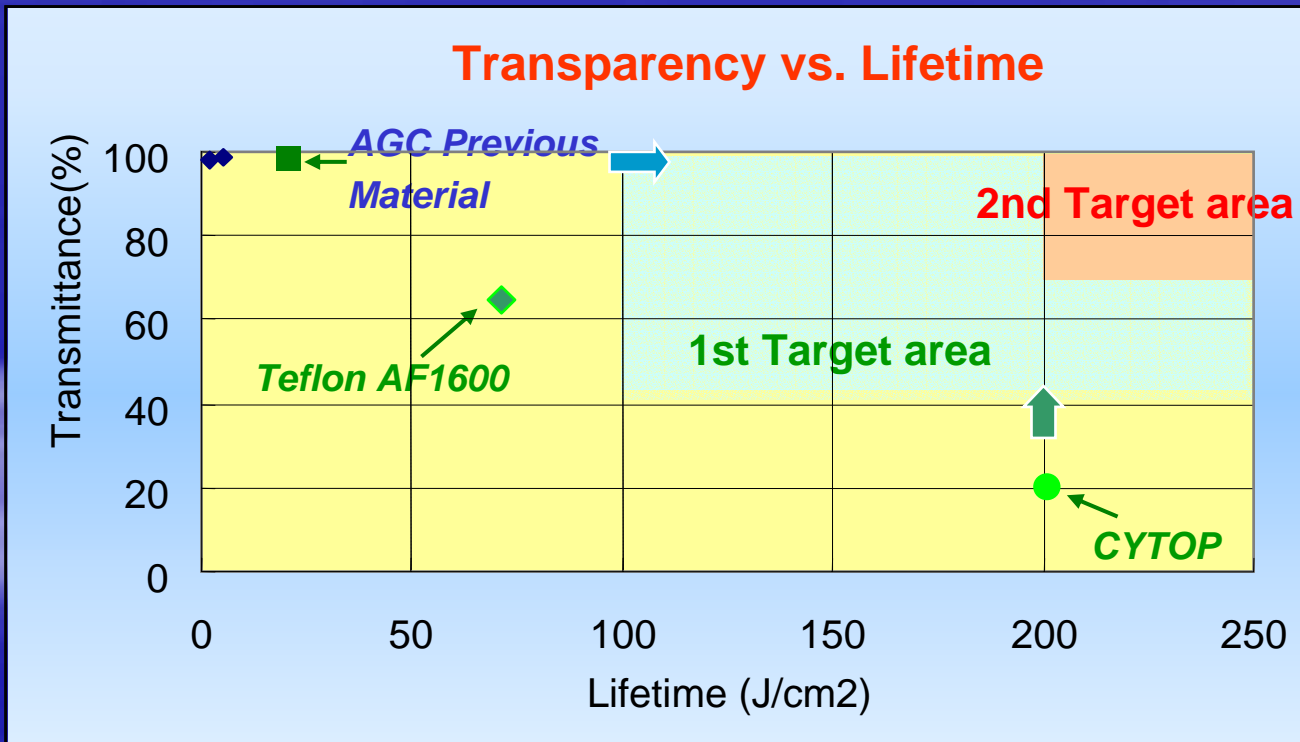
- Introduction
- Findings from Previous Works
- Our Strategy for New Polymers
- Experimental Results
- Conclusions and Future Plan

# Background



# Objectives and Target

Development of the material which has high transparency and outstanding durability to 157nm Laser



Required lifetime

Source: Paul A. Zimmerman et al, 4th 157 nm Symposium, Yokohama, Japan, 08/2003. Immersion-157 Litho Symposium

# Our findings from previous works

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1. Comparison of Perfluoro polymers and H-containing polymers
2. Effect of tertiary Hydrogen
3. Effect of substituent

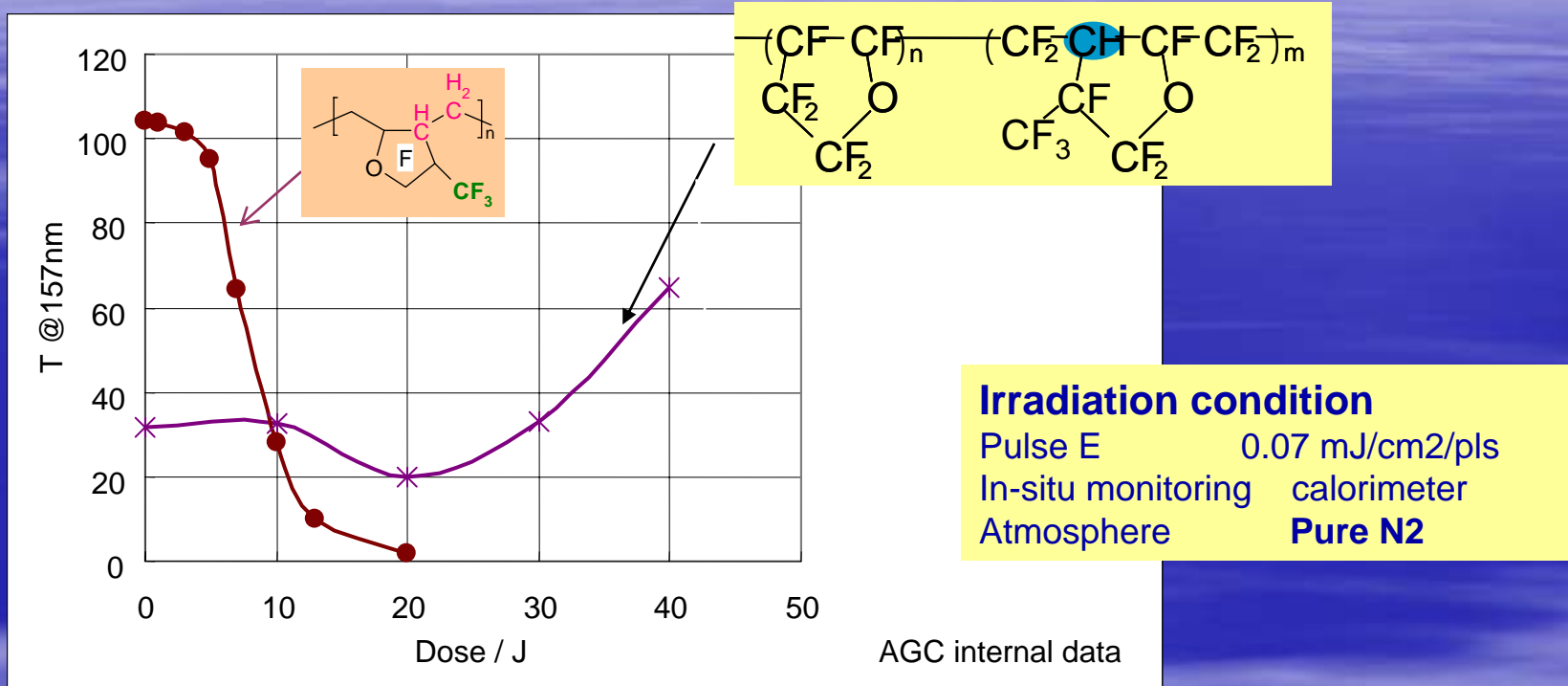
# Finding 1 : Comparison of Perfluoro and H-containing Polymers

	Perfluoro Polymer (CYTOP)	H-Containing Polymers (AGC material)	cf. PFPE (Fomblin)
Initial Transmittance	Low	High	High
Optical Durability	High	Low	High
Mechanical Durability	relatively High	Low	- (Oil or grease)

CYTOP and other type of polymer should be treated complementary

- O or H should be necessary to improve transmission of polymer
- Fluorine content should be maximized in the polymer main chain

# Finding 2: Unexpected effect of tert-H



Polymers that contain small number of tertiary hydrogen showed better performance.

# Presumption of tert-H effect

## Expected effects of tert-H

- 1) Minimum number of H      Less opportunity to react
- 2) Strong C-H bond      Slower H abstraction reaction

**→ H abstraction reaction is suppressed**

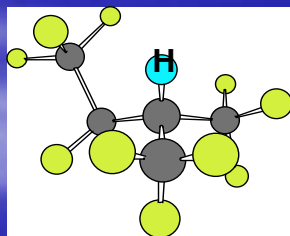
Ref. A.K.Chandra et.al. Int. J. Chem Kinet 35 130 (2003)  
 A.K.Chandra et.al. J.Phys.Chem. A 104 9244 (2000)

- Calculation of bond energies

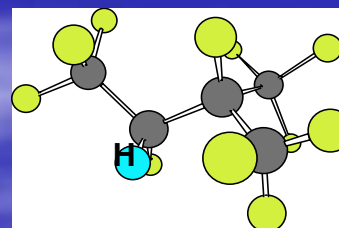
**Tertiary C-H(-CF<sub>2</sub>)<sub>3</sub>-CH)**

**Secondary CH (-CF<sub>2</sub>CHF<sub>2</sub>-)**

(model example :  
C<sub>5</sub>F<sub>11</sub>H)



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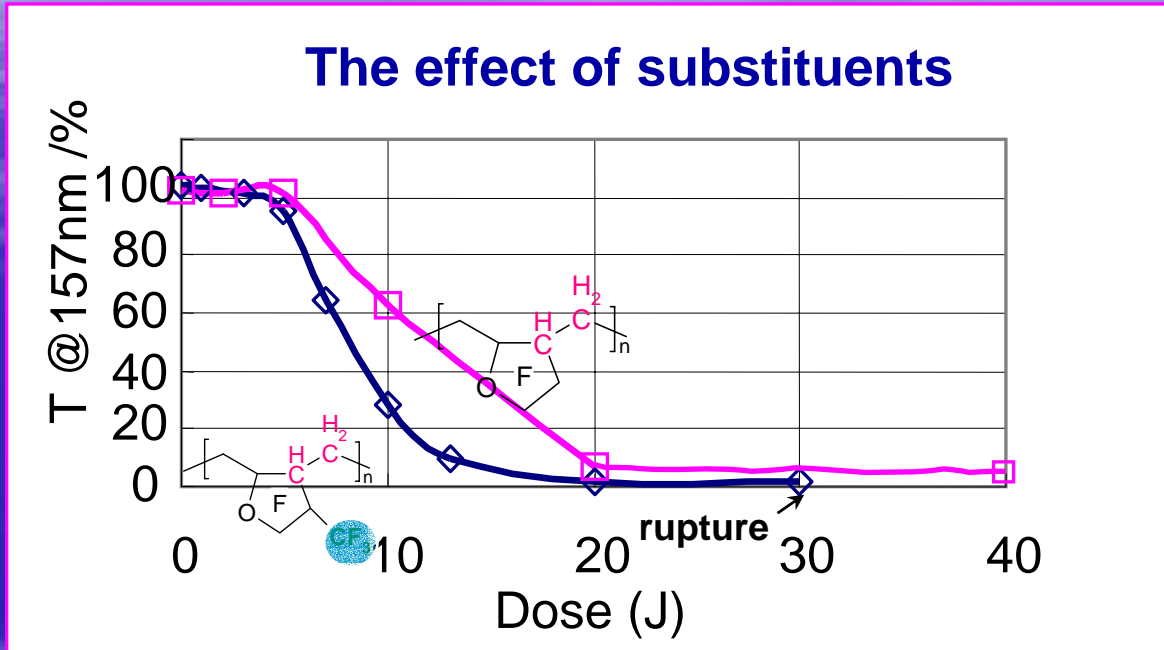


**100 kcal/mol**

**96 kcal/mol**

Estimated by  
 Ab initio theoretical  
 calculation  
 PBE1PBE/6-311+G(2d,p)  
 //B3LYP/6-311G(d,p)

# Finding 3: Effect of Substituents



AGC internal data

Existence of substituents such as CF3 units drops both mechanical and optical durability.

# Summary of Our findings

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- **CYTOP skeleton is suitable for high durability. Moreover, Fluorine content should be maximized as much as possible**
- **Tertiary hydrogen as well as ethereal oxygen (e.g. PFPE) improve the initial transmittance.**
- **Pendant group (e.g. CF<sub>3</sub>, CF<sub>2</sub>CF<sub>3</sub>) should be avoided in the polymer structure.**

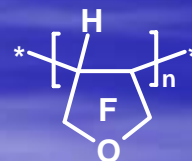
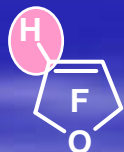
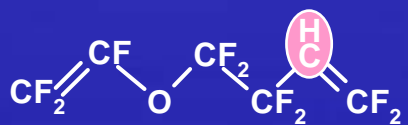
# Strategy for New Structure

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- CYTOP structure will be adopted as the platform to keep high durability.
- It should contain tertiary H or ethereal O in main chains to achieve high transmittance.
- Pendant groups (CF<sub>3</sub>, CF<sub>2</sub>CF<sub>3</sub> etc.) should be avoided for the improvement of durability.

# Our New Candidates

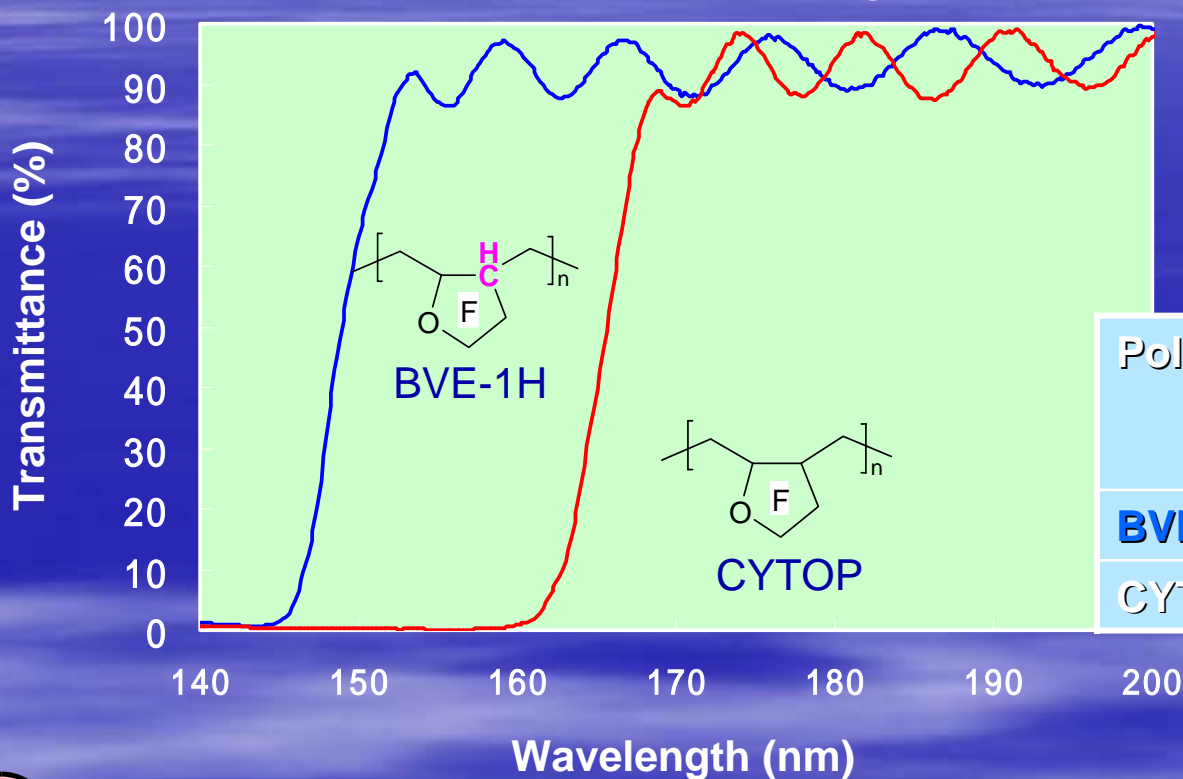
- Platform : CYTOP analogue
  - 5-membered rings which have one oxygen in the each rings.
- Tert-H or etheral O is needed to improve the transmittance.
  - Introduction of tertiary CH into main chain.



- Introduction of etheral oxygen into main chain.
  - Now under development
  - (It might need a different structure from CYTOP)

# Transmission of BVE-1H polymer

Transmission of Self-standing film at 1um



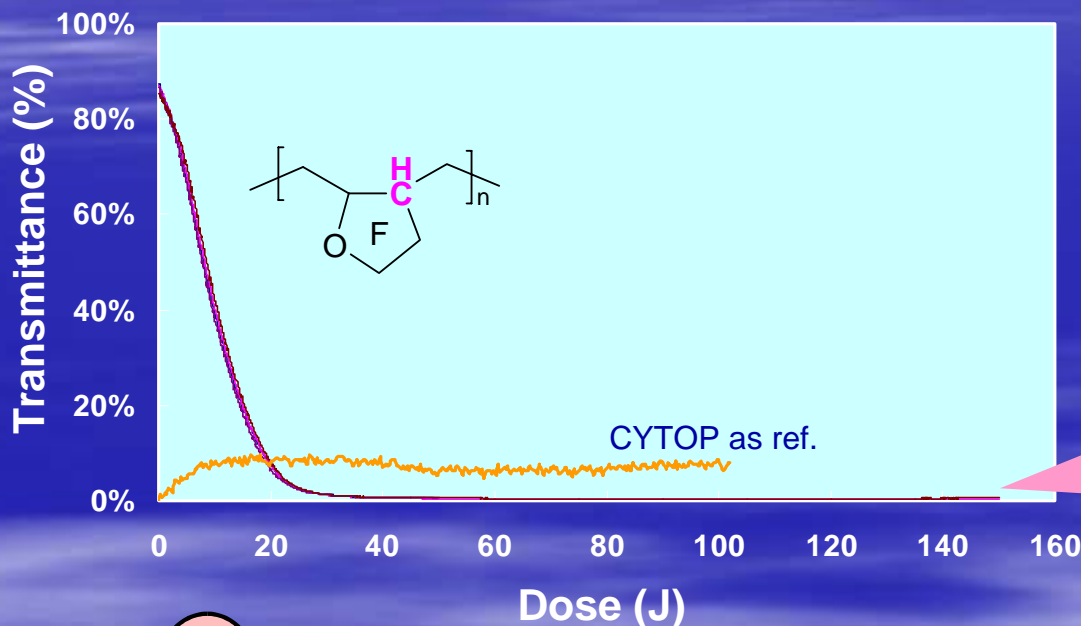
Polymer	ABS co- at 157nm <small>Base10</small>
<b>BVE-1H</b>	<b>0.02</b>
CYTOP	1.7



Shift of absorption edge was observed without significant deterioration of transmission

# Durability of BVE-1H

## In-situ Transmission



## Irradiation condition

Pulse E 0.05 mJ/cm<sup>2</sup>/pls  
 Frequency 1000Hz  
 In-situ monitoring calorimeter (Gentec)  
 Atmosphere **Pure helium<sup>\*1</sup>**

These data were collected by Selete



**The fracture was not observed after Air gun blow test**



Mechanical durability was significantly Improved.



Rapid transmission drop was observed.

<sup>\*1</sup> ; Please see the presentation of Dr.Sasaki (Selete) to understanding helium effect.

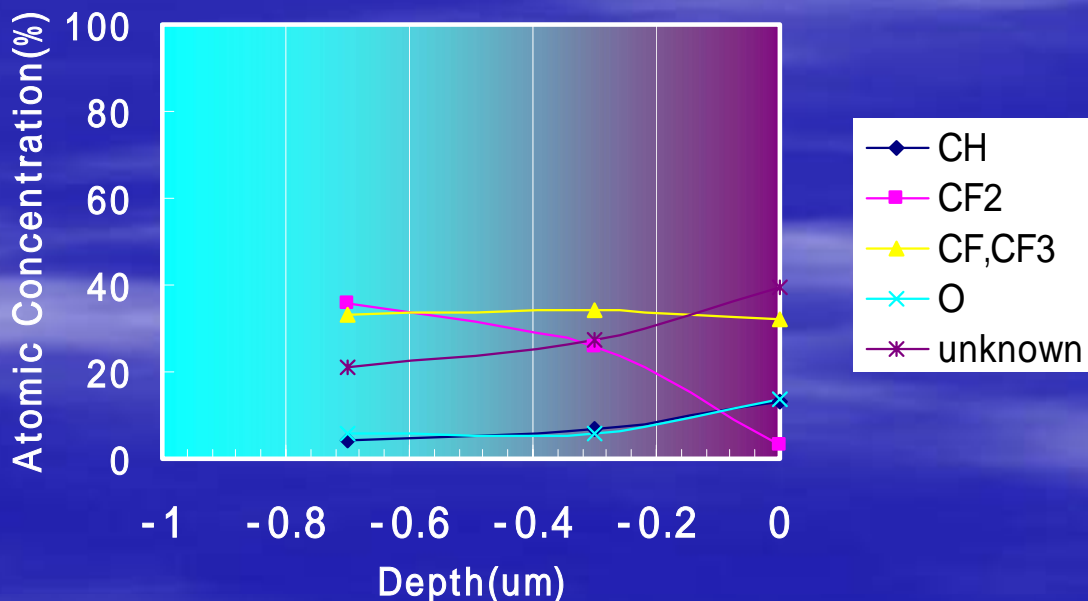
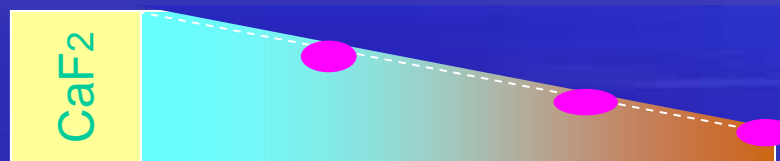
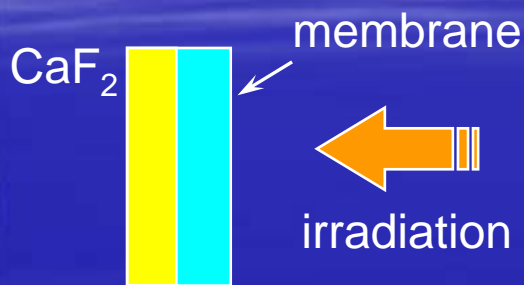
# Analyses of irradiated BVE-1H

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- FT-IR
  - COF and C=O or CF=CF are observed
  - CH is also observed after irradiation
- XPS analysis (Surface of Membrane)
  - Decrease of CF<sub>2</sub> and increase of CF and CF<sub>3</sub> are observed
  - Total amount of F decreased after irradiation.

# Depth profile of XPS analysis

In order to investigate element composition of the depth profile, we have irradiated the film deposited on CaF<sub>2</sub> substrate. After that, we cut sample diagonally then analyzed its surface.



# Analytical conclusions and Next step

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- Tert-CH survived after 150J irradiation
- It seems that decrease of CF<sub>2</sub> content shows crosslinking of the polymer.
- It seems that the control of crosslinking in the surface should be important.
- We need to much more attention paid to CF<sub>2</sub> configuration.

# Copolymerization of BVE-1H

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## Purpose

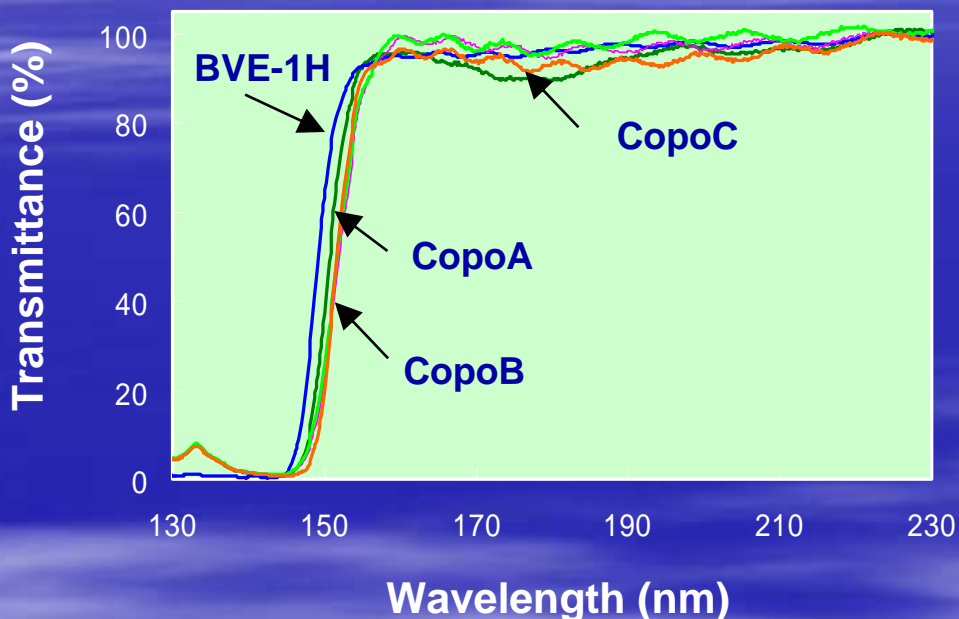
1. To reduce the total amount of CH by copolymerization
2. To investigate structure suppressing transmission



We have synthesized several kind of copolymers and evaluated their transmission.

# Copolymerization of BVE-1H

Transmission of film on CaF2 (at 1um)



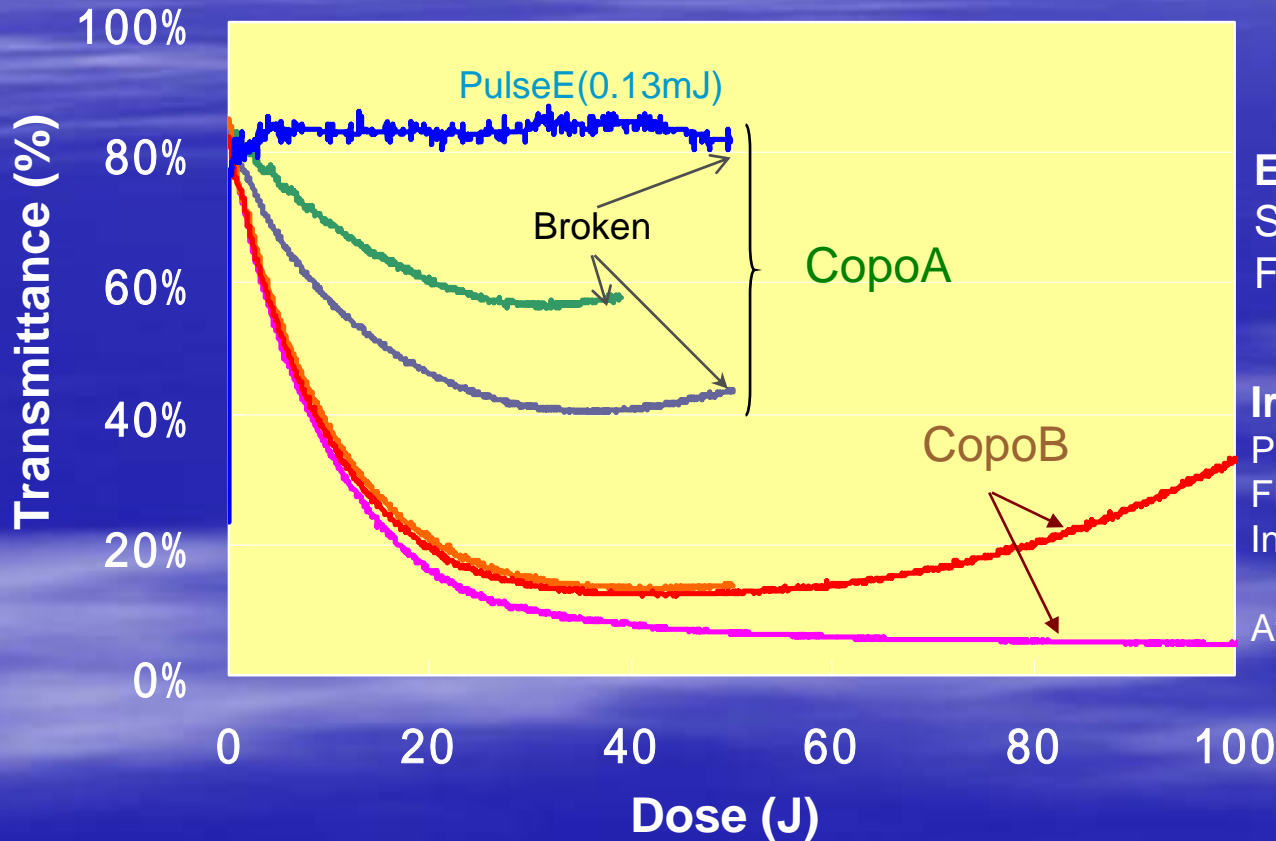
Polymer	ABS co- at 157nm base10
BVE-1H	0.022
CopoA	0.022
CopoB	0.016
CopoC	0.032



It succeeds in carrying out copolymerization without a drop of transparency.

# Durability of BVE-1H copolymers

## In-situ Transmission



**Experimental conditions**  
 Sample self-standing film  
 Film thickness about 1 $\mu$ m

**Irradiation conditions**  
 Pulse E 0.05 mJ/cm<sup>2</sup>/pls  
 Frequency 1000Hz  
 In-situ monitoring calorimeter (Gentec)  
 Atmosphere **Pure helium**

# Evaluation Results of BVE-1H copolymers

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- Some of copolymers showed better durability than BVE-1H
  - All samples after irradiation became so fragile, therefore mechanical durability was not enough.
  - The variation of results in the same samples is large.
- ➔ To achieve better performance.....
- ◆ Investigation of appropriate perfluoro-comonomer
  - ◆ Optimization of composition of copolymer
  - ◆ Modification of purification method

# Conclusion and future plan

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- We have found some key strategies to improve the durability.
- We have synthesized some polymers along with the above guideline. In our experiments, tert-CH showed good mechanical durability as expected. Moreover, we have found some possibilities to improve their optical durability.
- We will also focus on developing other types of fluoropolymer to achieve longer lifetime. (e.g. ethereal oxygen containing polymer)

**We have found out a certain material, that has suitable Tg for making membrane. Increasing of molecular weight is a issue for obtaining good mechanical strength.**

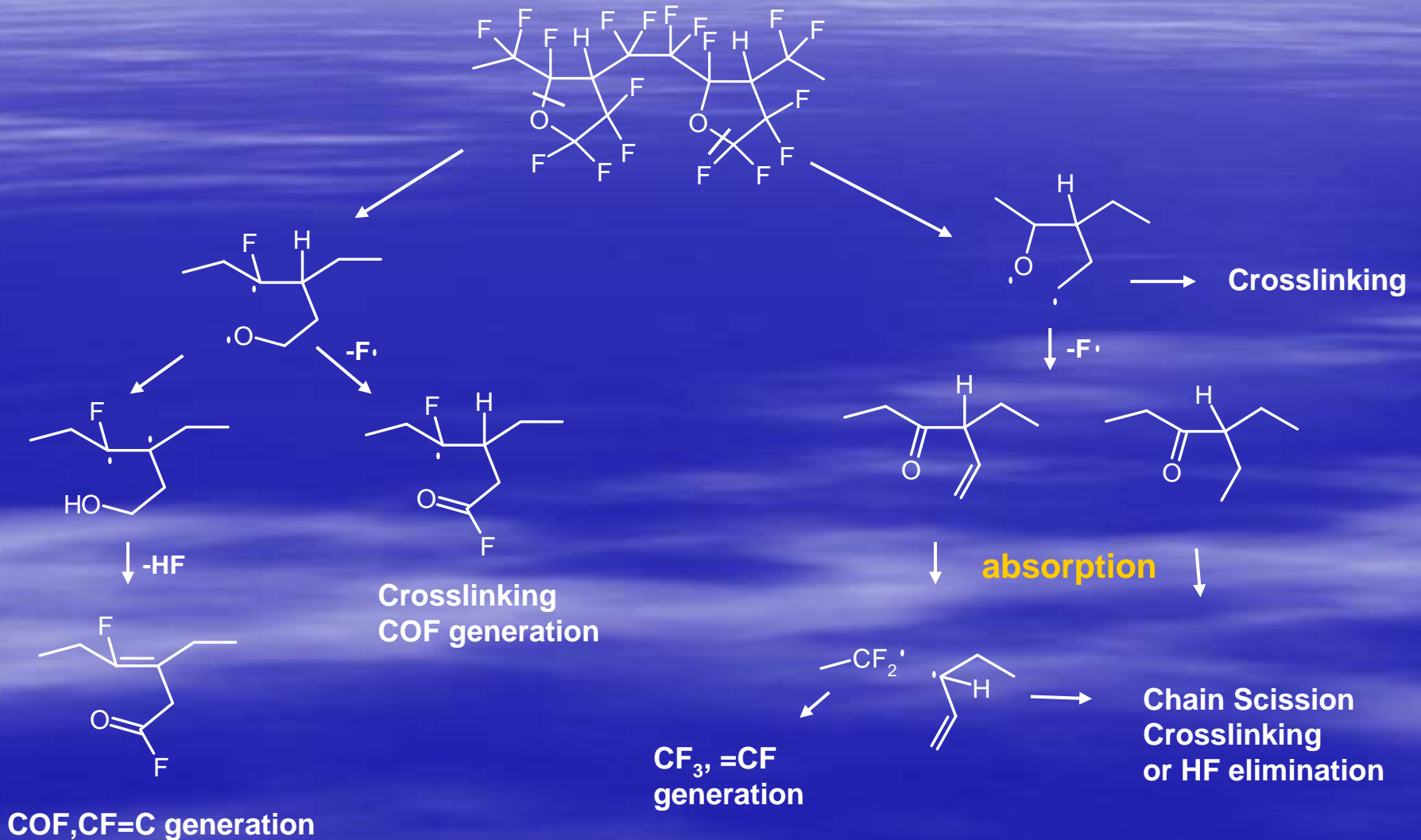
# Acknowledgements

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- Komatsu Ltd - for evaluation of polymer durability
- Jun Irisawa, Asahi Glass – for simulation support

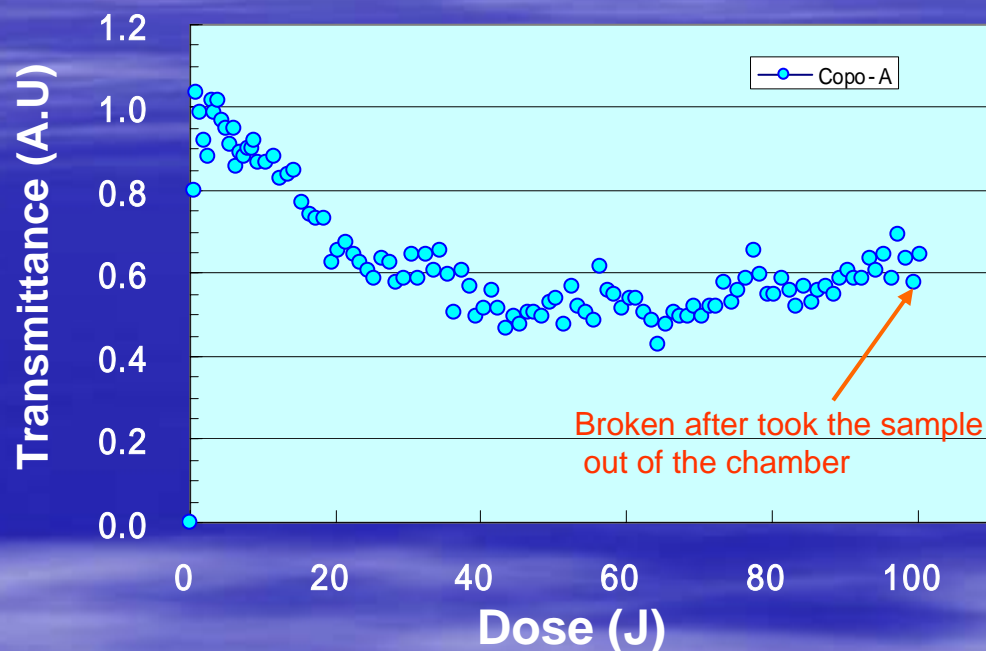
# Appendix

# Possible Photodegradation Pathways of BVE-1H



# Durability of BVE-1H copolymer A (Our Latest internal Data)

Transmission ratio from initial



## Experimental conditions

Sample self-standing film  
Film thickness about 1 $\mu$ m

## Irradiation conditions

Pulse E 0.1 mJ/cm<sup>2</sup>/pls  
Frequency 200Hz  
In-situ monitoring calorimeter  
Atmosphere **N<sub>2</sub>(O<sub>2</sub><10ppm)**

AGC internal Data

Slight change of coating process gave such a result. On the other hand, a clear change was not observed in the mechanical property.