

Ring Opening Metathesis Polymerization for 157 nm Photoresists

Brian Osborn
September 11, 2001



The California Institute of Technology

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Ring Opening Metathesis Polymerization (ROMP)

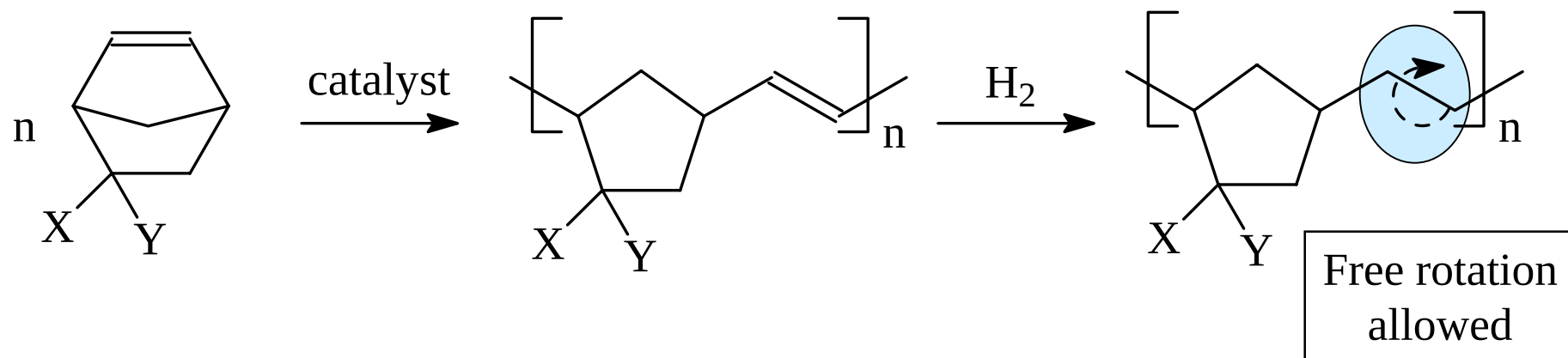
Advantages

- Low catalyst loading (< 50 ppm), therefore little residual metal (Ru)
- Polymerizes geminally disubstituted norbornenes
- Robust catalyst, functional group and water tolerant
- Molecular weight can be controlled



Geminally Disubstituted Norbornenes

ROMP catalysts easily polymerize key monomers:



Problem: T_g too low ($\sim 25\text{-}30^\circ\text{C}$) for norbornenes



Routes to High T_g ROMP Polymers

- **The 193 nm System Approach**

Incorporation of dinorbornene and carboxylic acid (-COOH) in the polymer composition increases the polymer's T_g

- **One problem, however:**

Dissolution rate increases rapidly with acid loading

- **The 157 nm solution:**

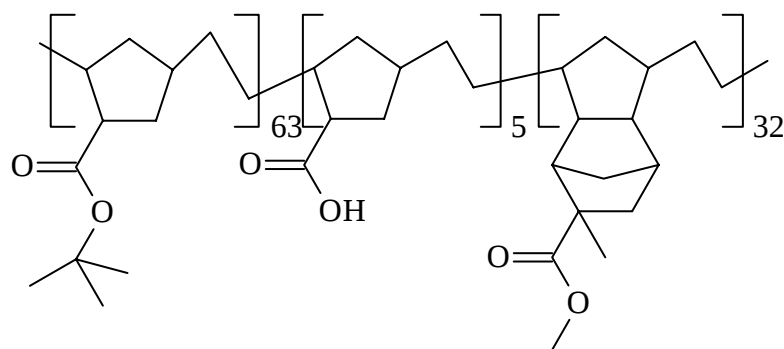
Use dissolution inhibitors to slow dissolution rate of the base polymer and also alleviate swelling¹

¹Ito, H.; Allen, R. D.; Opitz, J.; Wallow, T. I.; Truong, H. D.; Hofer, D. C.; Varanasi, P. R.; Jordhamo, G. M.; Jayaraman, S.; Vicari, R.; *Proc. SPIE* **2000**, 3999, 2.



Routes to High T_g ROMP Polymers

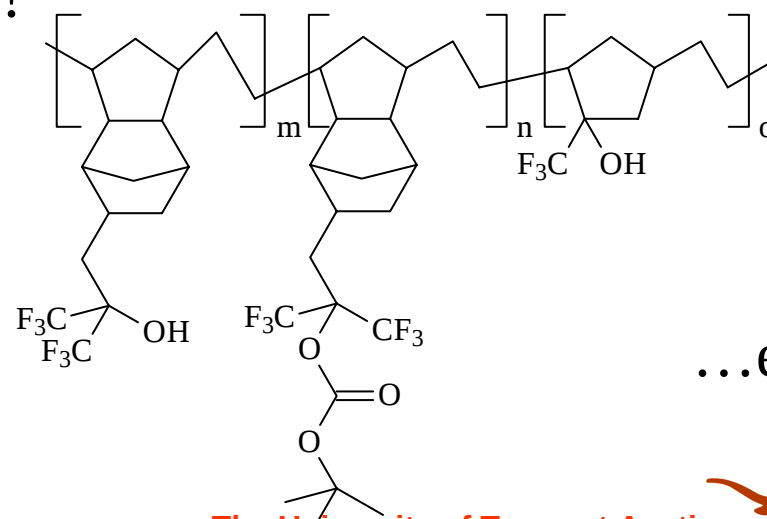
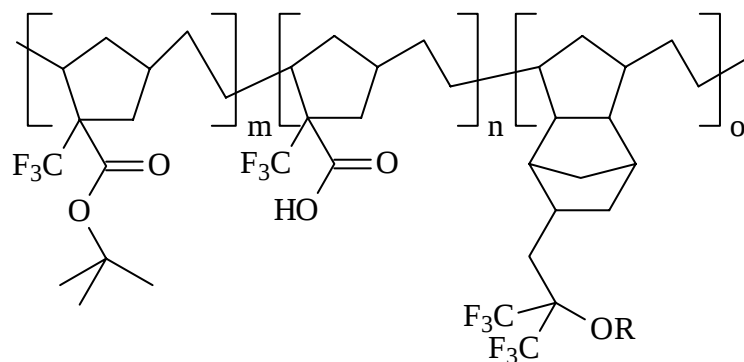
193 nm System - Tsutomu Shimokawa, Kyle Patterson, et al.



T_g : 132 °C

Higher T_g due to hydrogen bonding between acid and ester groups in polymer

157 nm Analogs – Many Possible!



...etc.



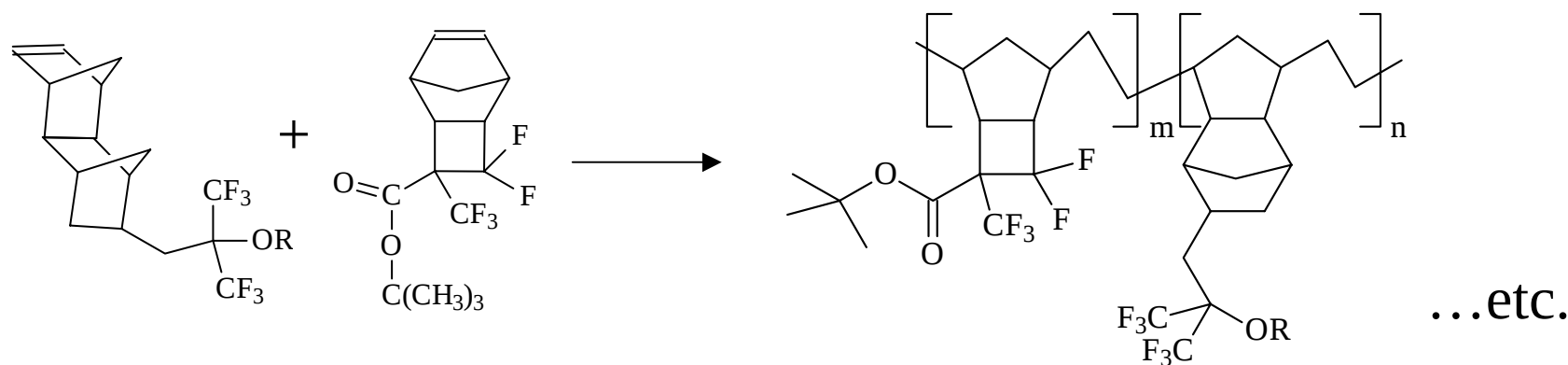
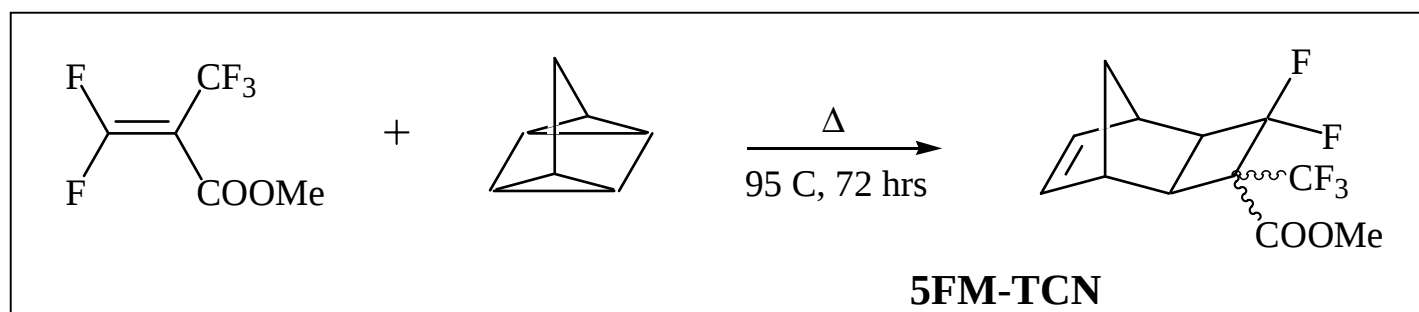
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Routes to High T_g ROMP Polymers

TriCycloNonene (TCN) Copolymers

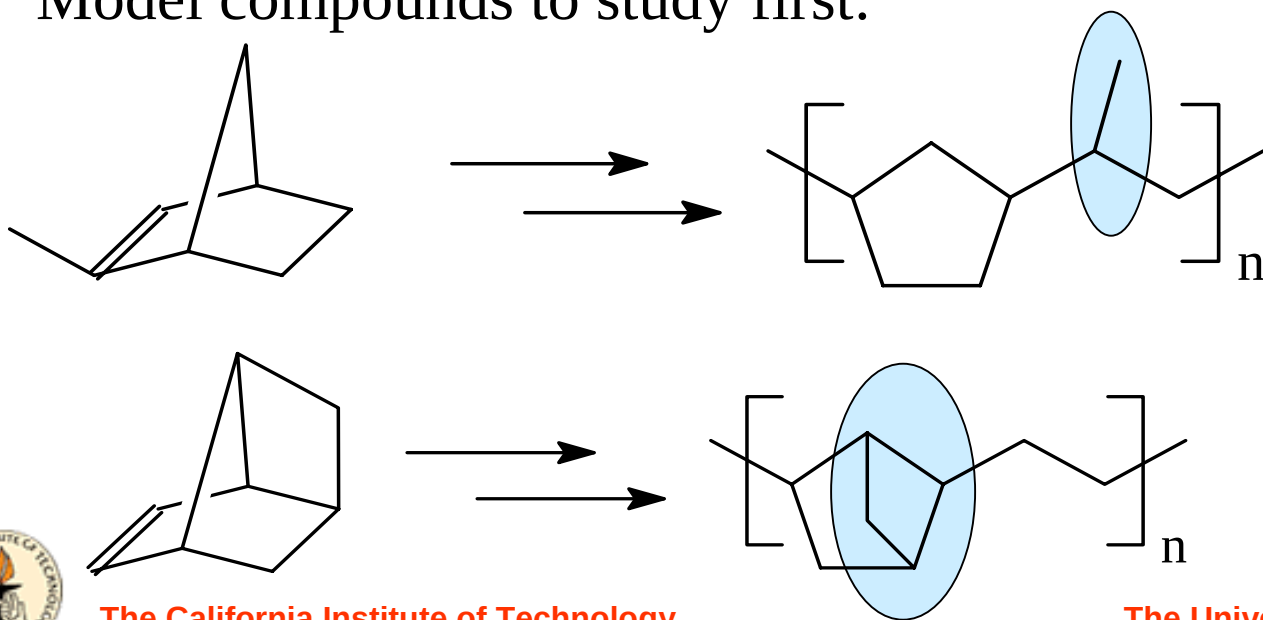


Routes to High T_g ROMP Polymers

New comonomers:

Exploration of new norbornene monomers with increased steric bulk to make hydrogenated polymer backbone less flexible.

Model compounds to study first:



Added steric bulk may restrict rotation

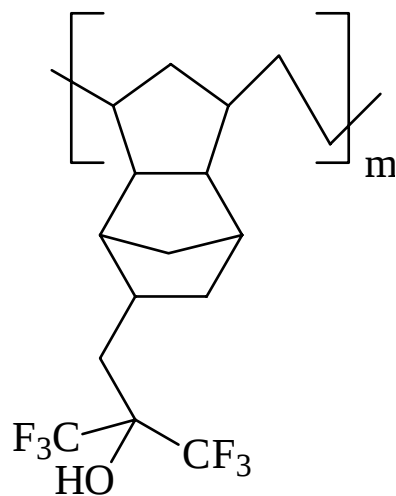


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Initial Synthesis Successful

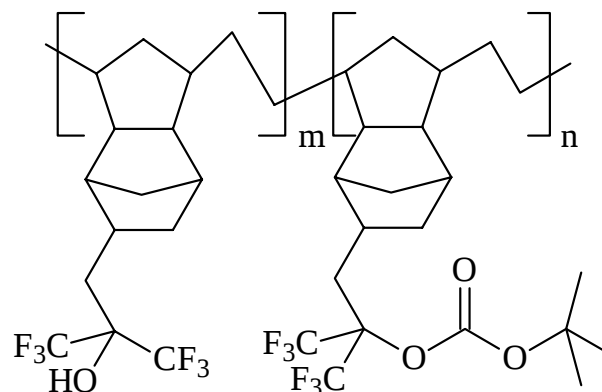
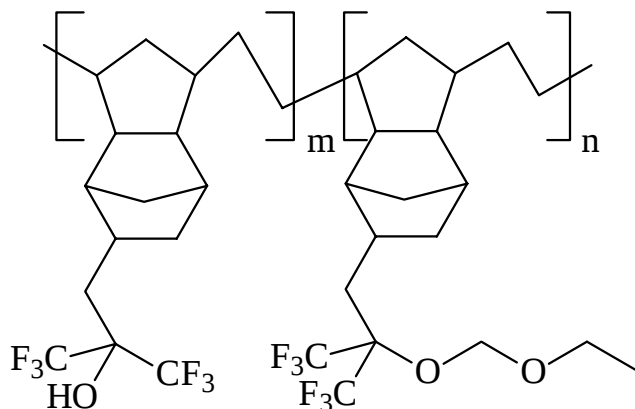
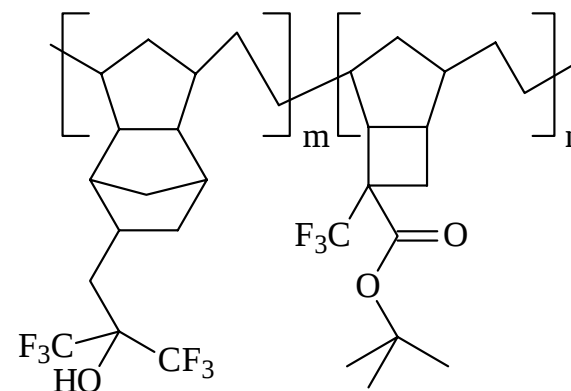
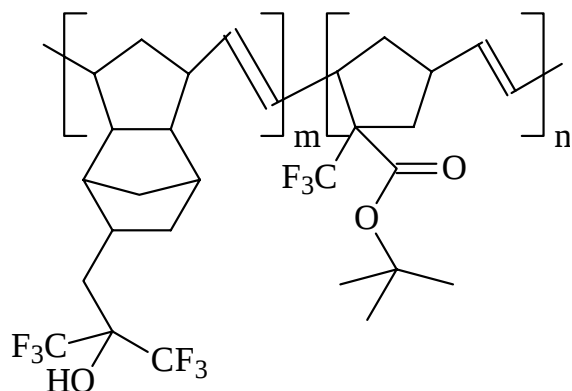


DiNorbornene HexaFluoroisopropyl Alcohol
(DNHFA)

- T_g is 85-90 °C after hydrogenation
- Abs. @ 157 nm: $3.3 \mu\text{m}^{-1}$ (first pass)
- Absorbance is higher than expected
 - Polymer requires improved purification



New Dinorbornene ROMP Polymers



ROMP Summary

- Dinorbornene copolymers look promising
- First TCN ROMP copolymers are completed

Future Work

- Fully characterize new polymers
- Continue ROMP copolymer synthesis
- Initial imaging experiments



Acknowledgments

- Daniel Sanders (CalTech)
- Raymond Hung
- Takashi Chiba
- Dr. Tsutomu Shimokawa (JSR)
- Dr. Kyle Patterson (Motorola)
- Central Glass
- Clariant
- JSR
- SEMATECH



Metal Catalyzed Vinyl Addition Polymerization for 157 nm Photoresists

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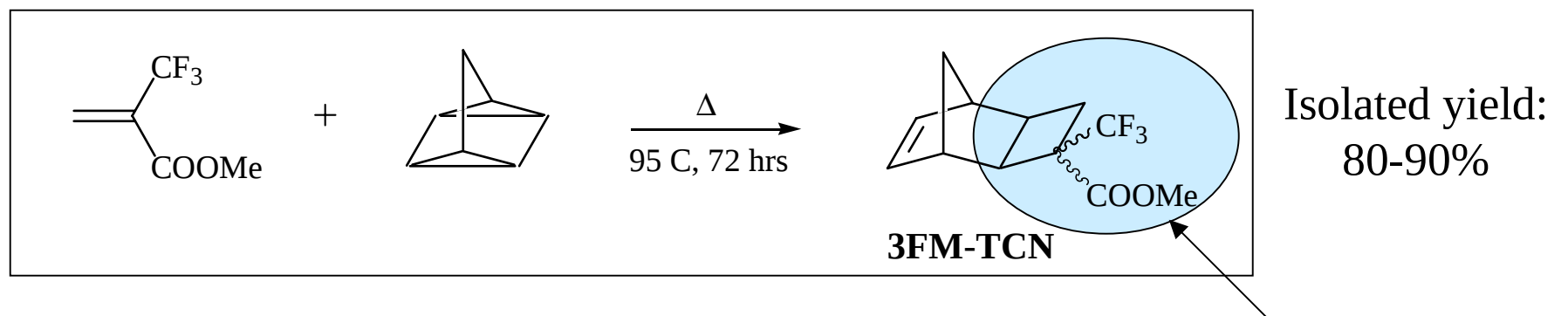


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Metal (Pd^{+2}) Catalyzed Vinyl Addition Polymerization – 3F-TCN Platform

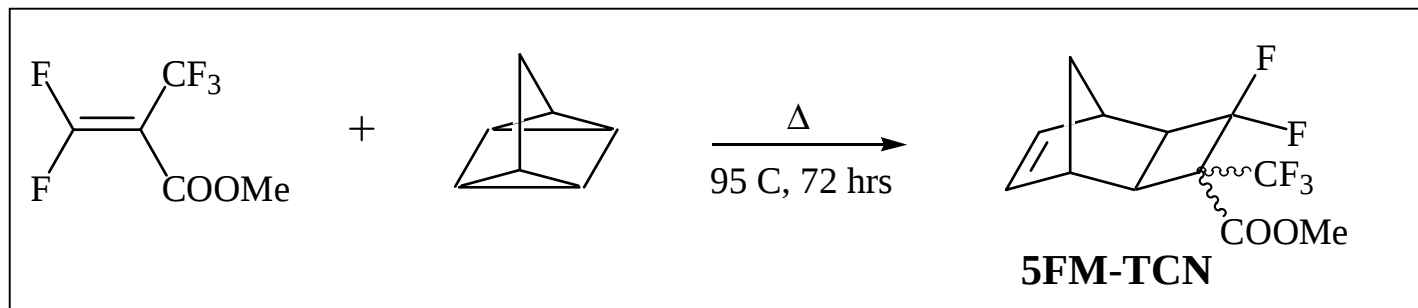


- Clean reaction
- High yield
- Easy purification
- Allows use of a transparent ester as a solubility switch
- Successfully polymerizes via metal catalyzed vinyl addition

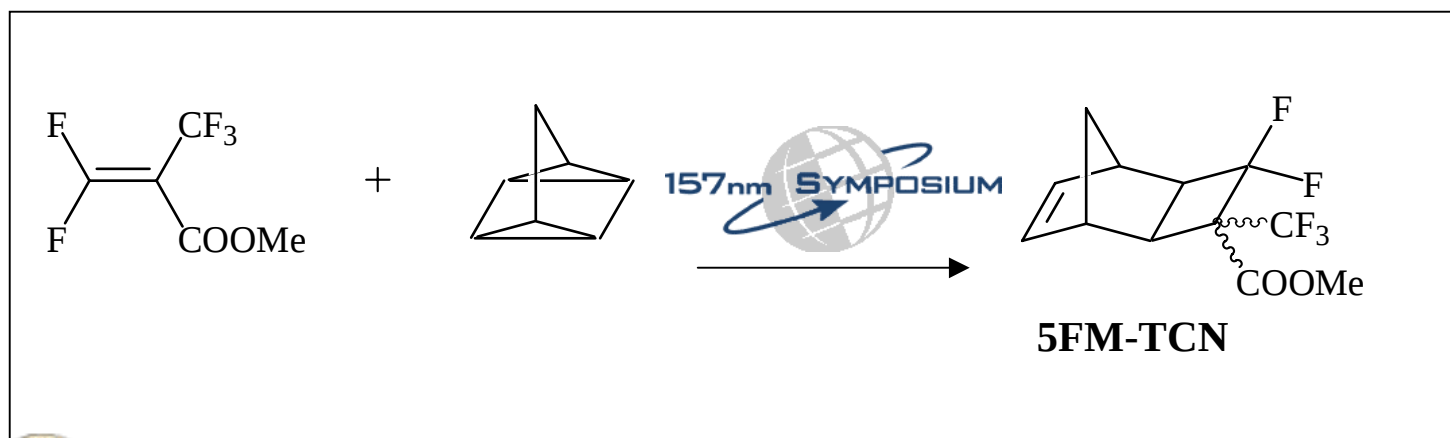
Geminally disubstituted functional groups moved away from olefin



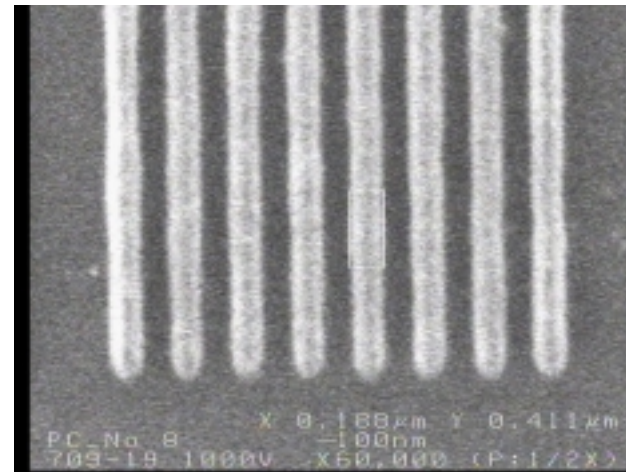
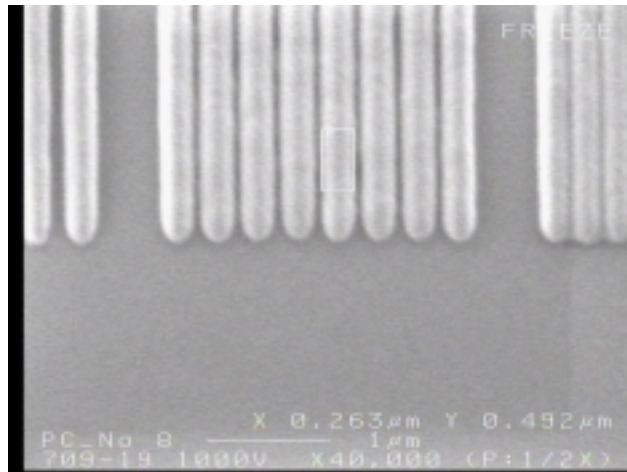
Synthesis of 5F-TCN Monomer



Higher fluorine content lends *lower* absorbance at 157 nm
...but lower yields.



Initial 3F-TCN-co-NBHFA Images



No dissolution inhibitor. Dissolution inhibitor added.

3F-TCN copolymer images have very poor contrast, until
dissolution inhibitor (DI) added.



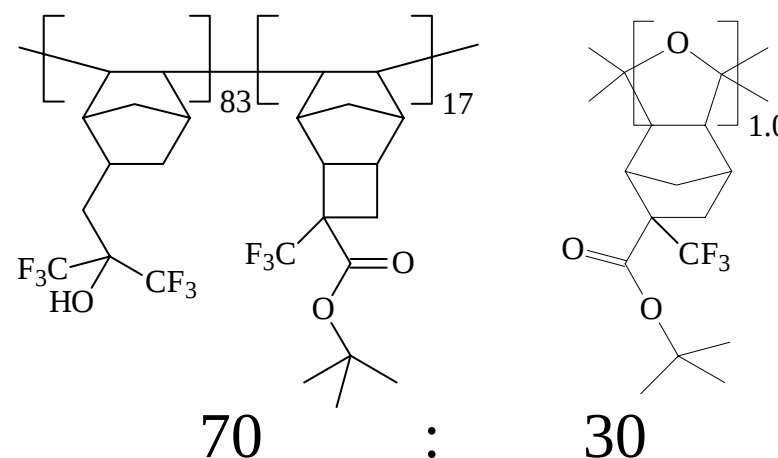
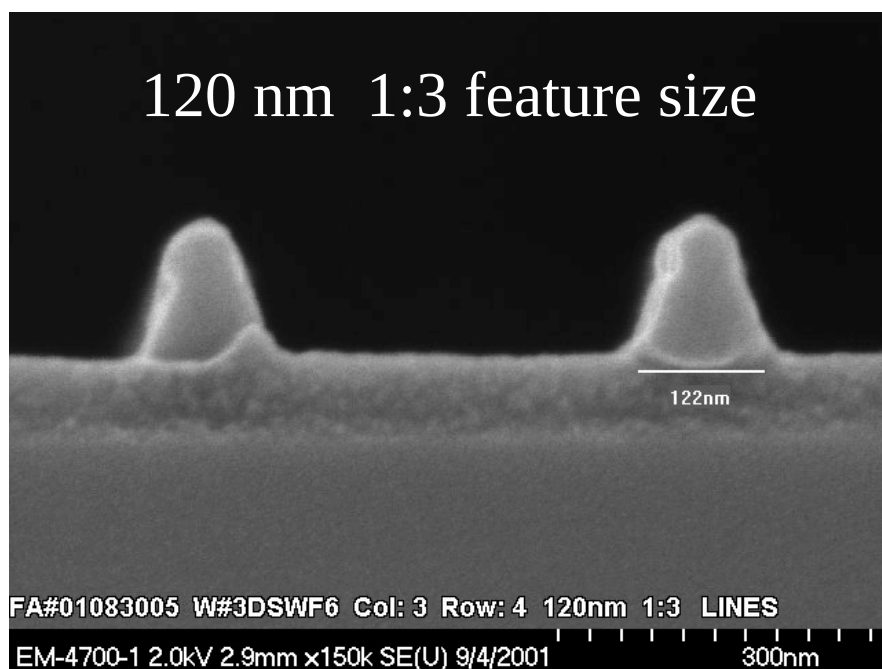
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3F-TCN-co-NBHFA - *Binary Mask*

A 70:30 blend of polymer and dissolution inhibitor.



BPO-R-007-A
 70:30 polymer:DI blend
 6% TPS-Nf, 0.3% TBAH
 148.9 nm poly on 81.9 nm G0
 0.7 σ aperture, binary mask
 PAB: 140 °C/60 s, PEB: 130 °C/90 s
 60 s development in 0.26 N TMAH
 DOSE: 19.0 mJ/cm² FOCUS: 0.0 nm

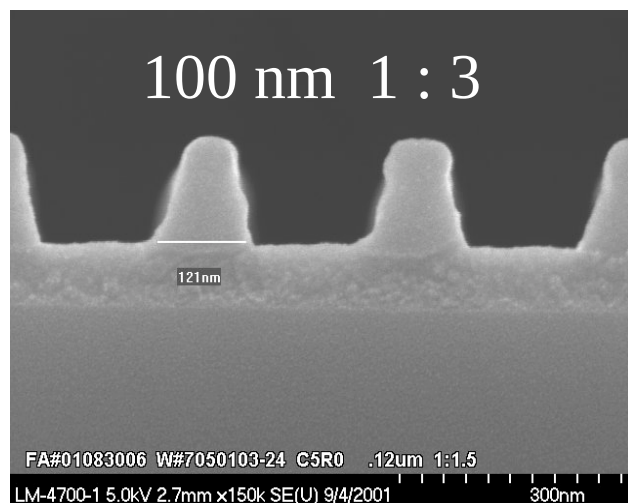
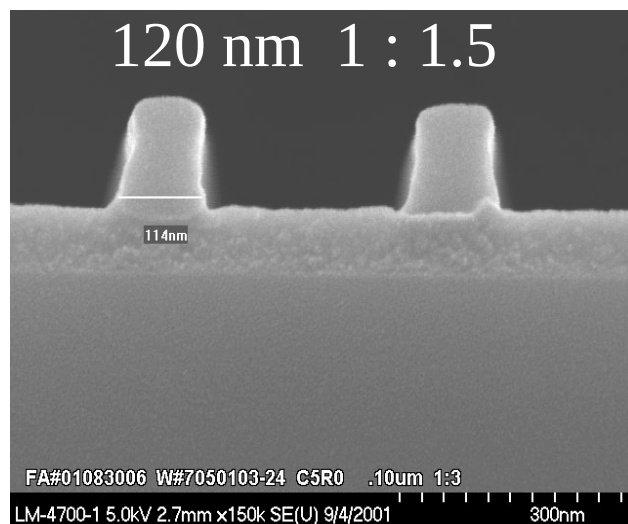


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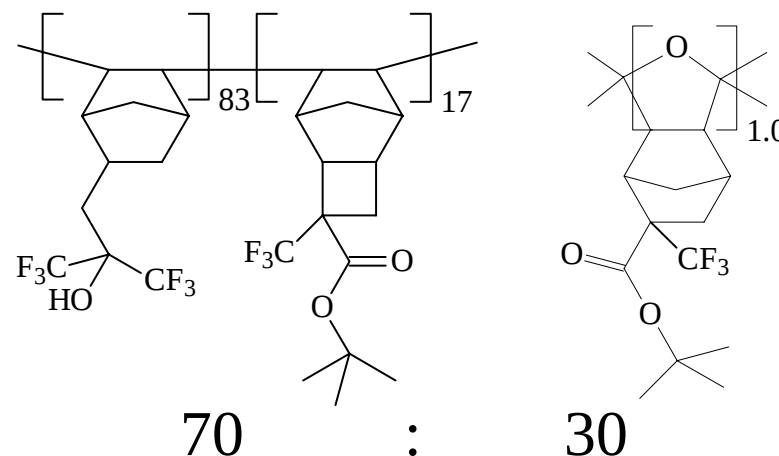
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3F-TCN-co-NBHFA - *Phase Shift*



Changing mask to a **strong phase shift** mask results in superior feature profiles, and smaller resolution possible.



BPO-R-009-A 70:30 polymer:DI blend
 6% TPS-Nf, 0.3% TBAH
 145.6 nm poly on 82.4 nm G0
 0.3 σ aperture, phase shift mask
 PAB: 140 °C/60 s, PEB: 130 °C/90 s
 20 s development in 0.26 N TMAH
 DOSE: 39.0 mJ/cm² FOCUS: 0.0 nm



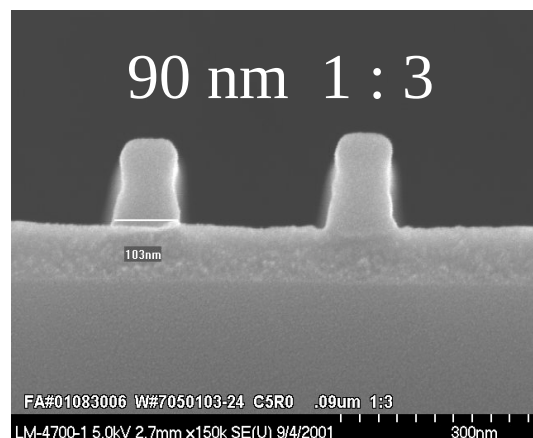
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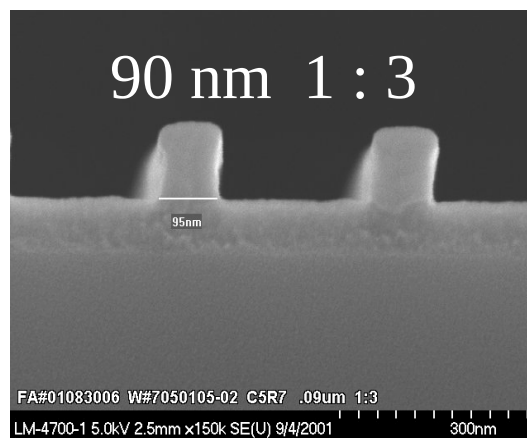


3F-TCN-co-NBHFA - *Phase Shift*

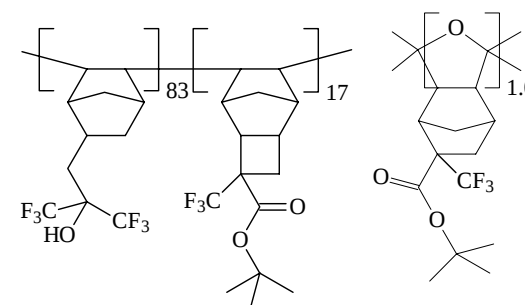
PEB 130 °C, 90 s



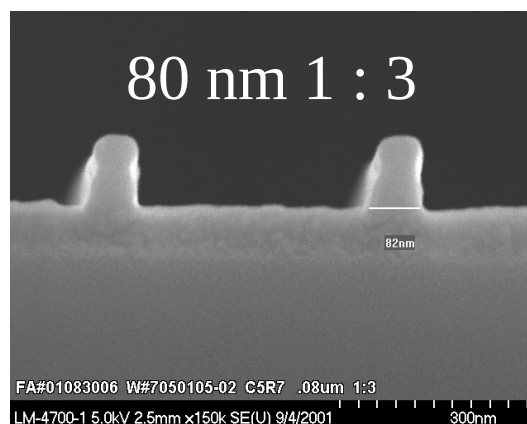
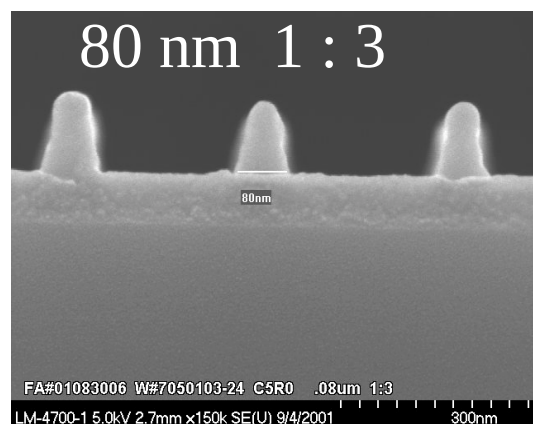
PEB 130 °C, 120



PEB temperature window appears large



70 : 30



BPO-R-009-A
 70:30 polymer:DI blend
 6% TPS-Nf, 0.3% TBAH
 145.6 nm poly on 82.4 nm G0
 0.3 σ aperture, phase shift mask
 PAB: 140 °C/60 s, PEB: 130 °C/120 s
 20 s development in 0.26 N TMAH
 DOSE: 39.0 mJ/cm² FOCUS: 0.0 nm

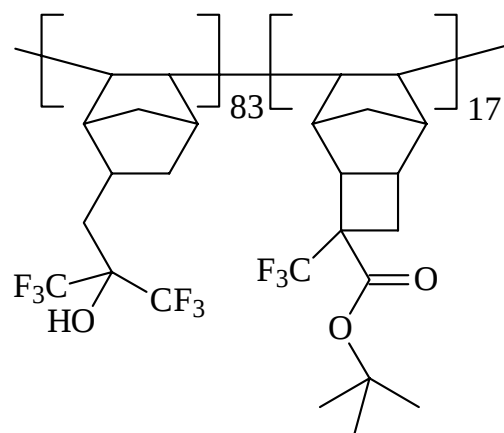


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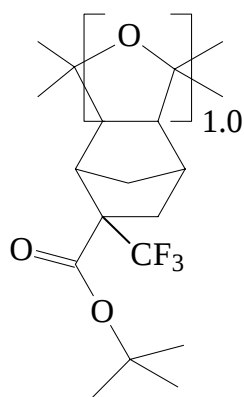
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Transparency Improvements to TCN Platform



Base polymer



Dissolution inhibitor

And,
6% TPS-Nf (PAG)
0.3% TBAH (base)
for total formulation

Base polymer absorbance
@ 157 nm: $2.0 \mu\text{m}^{-1}$

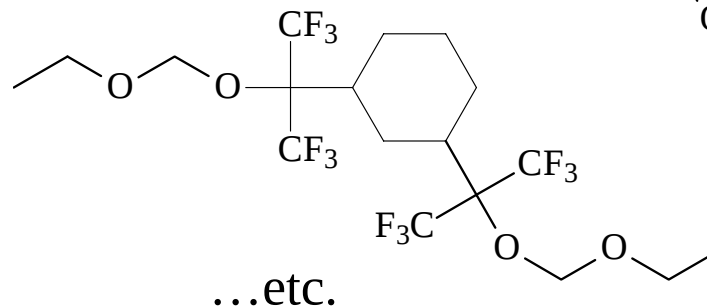
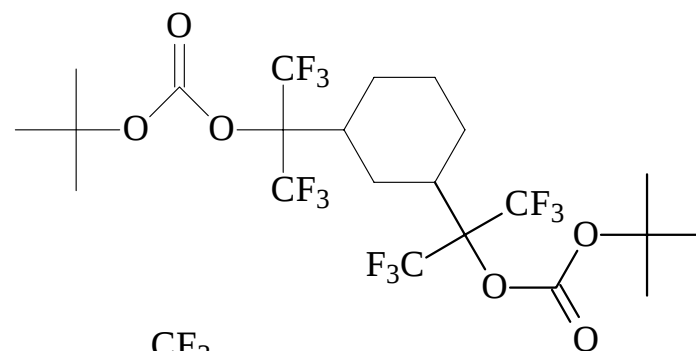
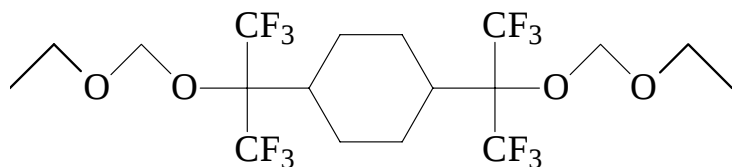
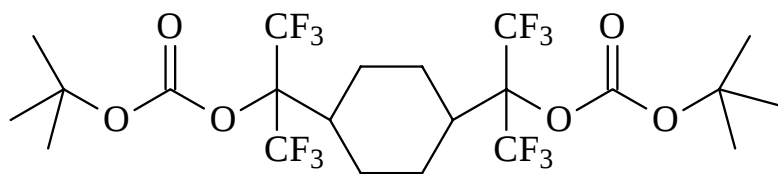
Formulated resist absorbance
@ 157 nm: $2.7 \mu\text{m}^{-1}$

Dissolution inhibitor has **strong impact on absorbance!**

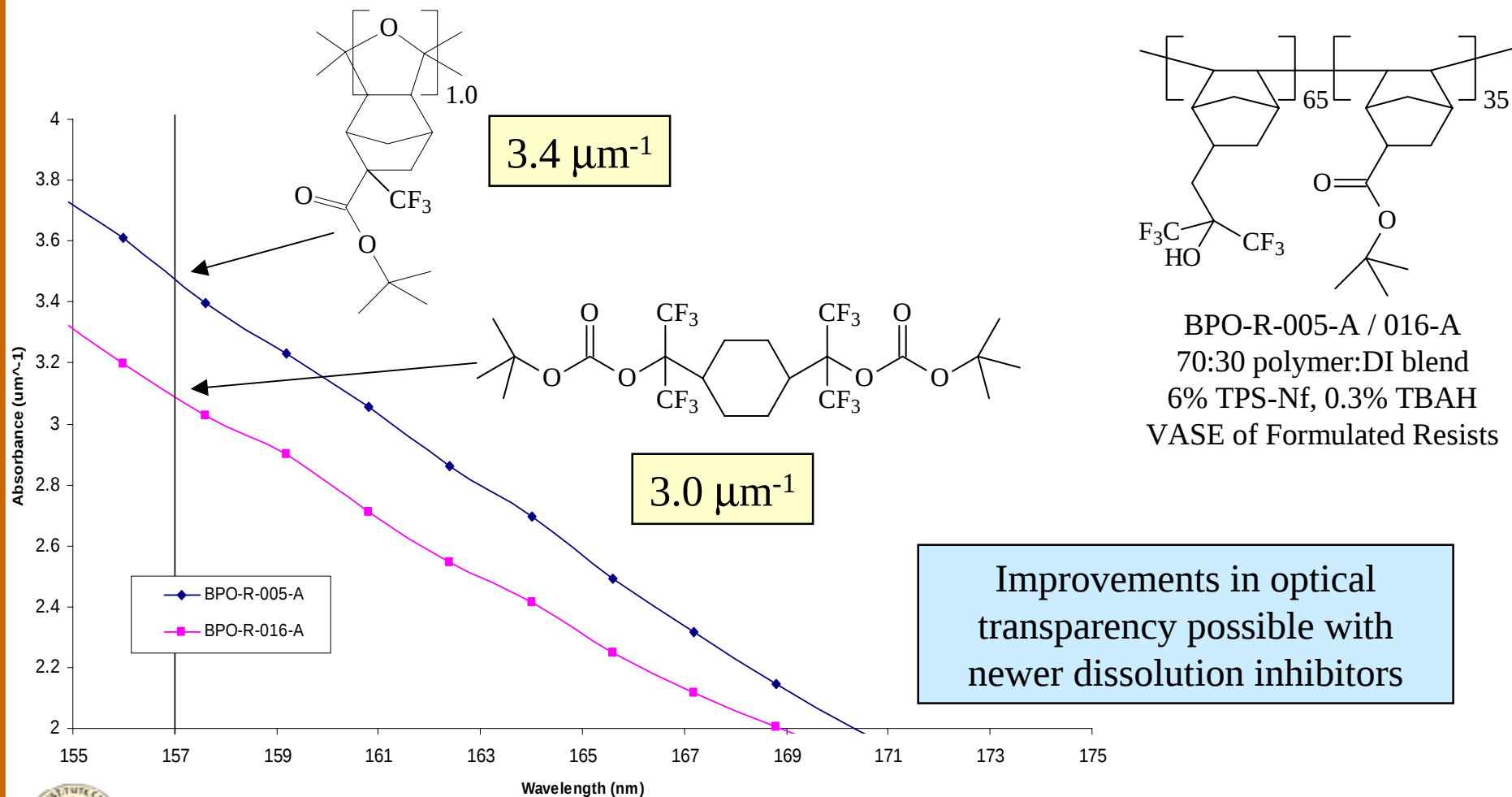


Transparency Improvements to TCN Platform

Polymer absorbance is relatively low, therefore better imaging requires use of new, **more transparent dissolution inhibitors**



Improvement in Transparency of Resist Formulated with Dissolution Inhibitors



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Conclusions and Future Work

- 3F-TCN-co-NBHFA platform shows very promising resolution in preliminary imaging studies,
- A limiting factor is the need to use more transparent dissolution inhibitors.
- Dissolution inhibitor strongly impacts image profile because of both improved contrast and changes in absorbance
- Recreate high yielding 5F-TCN monomer synthesis ...does this mean a trip to California??
- Start imaging work on 5F-TCN-co-NBHFA copolymer
- Evaluate more transparent dissolution inhibitors



Acknowledgments

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