Synthesis of alicylic polymers for 157 nm photoresists by Pd^{2+} catalyzed vinyl addition polymerization

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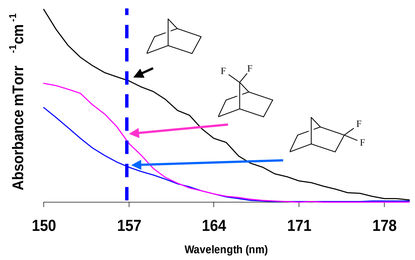
Introduction:

The development of 157 nm photoresists is proceeding at a frenzied pace. Many relatively transparent fluorocarbon monomers have been synthesized and studied and a variety of polymerization methods have been reported.[1] This poster reports the synthesis of a 157 nm resist platform[2] based upon alicylic polymers synthesized by allyl palladium catalyzed addition polymerization. One of the major advantages in using palladium catalysts is the ability to produce polymers with low and controlled molecular weights. However, one challenge in synthesizing functionalized alicyclic polymers for photoresists by cationic palladium catalysts is the cleavage of the acid labile *t*-butyl ester protecting group by strong acid that is generated during the polymerization. We have found that polymer-bound, sterically hindered pyridines, or "proton sponges", can be utilized to neutralize residual acid without decreasing the catalyst activity and the proton sponge easily removed by simple filtration after the polymerization. Poly (bicyclo[2.2.1]hept-5-ene-2-carboxylic acid *tert*–butyl ester-*co*-bicyclo[2.2.1]hept-5-ene-2-(1,1,1-trifluoro-2-trifluoromethylpropan-2-ol)) was successfully polymerized by palladium catalysis with proton sponges. Imaging work with this polymer system will be discussed.

1. (a) Chiba, T.; Hung, R.; Yamada, S.; Trinque, B.; Yamachika, M.; Brodsky, C.; Patterson, K.; Vander Heyden, A.; Jamison, A.; Lin, S. H.; Somervell, M.; Byers, J.; Conley, W.; Willson, C. G. *J. Photopolym. Sci. Technol.* **2000**, *13*, 657-664. (b) Ito, H; Wallraff, G. M.; Brock, P.; Fender, N.; Truong, H.; Breyta, G.; Miller, D. C.; Sherwood, M. H.; Allen, R. D. *Proc. SPIE* **2001**, 4345-31.

2. Hung, R. J.; Tran, H. V.; Trinque, B. C.; Chiba, T.; Yamada, S.; Sanders, D. P.; Connor, E. F.; Grubbs, R. H.; Klopp, J.; Frechet, J. M. J.; Thomas, B. H.; Shafer, G.; DesMarteau, D. D.; Conley, W.; Willson, C. G. *Proc. SPIE* **2001**, 4345-43.

Selective Fluorination of Norbornane

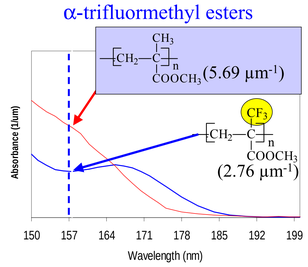


Geminal substitution at the two carbon bridge is the most effective fluorination pattern

T. Chiba, et. al., J. Photopolym. Sci. Technol **,** *13 (2000) 657-664*

Carboxylic Acids can be Acidic Groups for 157 Resist

α-trifluormethyl esters



Addition of α-CF_3 group reduces the absorbance of ester at 157 nm

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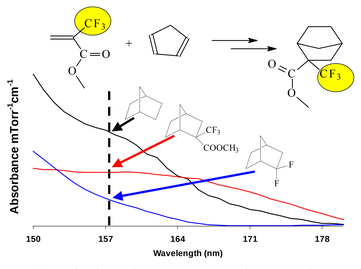
Gas-Phase UV Measurement of the α-CF3 substituted norbornane



The α-CF_3 substituted norbornane – improved transparency

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Polymers for Imaging at 157 nm

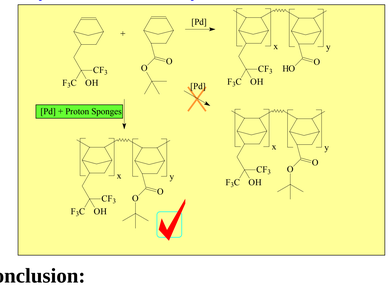
Unfortunately, we can not copolymerize these transparent monomers

↓

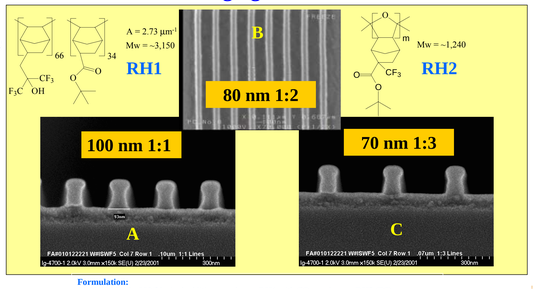
Compromise with the less transparent monomer for imaging

RH1

Pd^{2+} Catalyzed Addition Polymerization with Proton Sponges



Imaging Results



Formulation:
A: 50/50 blend of 80/20 vinyl addition copolymer **RH1** with CO copolymers **RH2 (DI)**
B, **C**: 70/30 blend of 70/30 vinyl addition copolymer **RH1** with CO copolymers **RH2 (DI)**
Conditions:
157 nm exposure (0.6NA-0.3σ, 50 mJ/cm²), phase shift mask, 148 nm thick resist on 70 nm anti-reflective layer (DUV30), 140°C-60s PAB, 130°C-90s PEB, 20 sec 0.26N TMAH development.

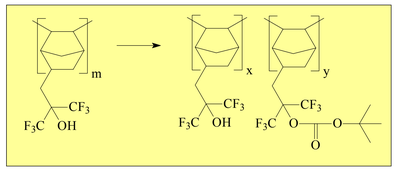
Conclusion:

The preliminary imaging results are encouraging, but it is clear that the transparency (2.78 μm^{-1}) of this polymer is far from perfect. It incorporates as much as 35% of the opaque NBTBE. In order to lower the absorbance of the polymer, the opaque monomer must be substituted with a far more transparent one. Unfortunately, the relatively transparent CF_3-NBTBE could not be polymerized by cationic Pd^{2+} catalyst. This monomer has to be modified in order to be polymerized by Pd^{2+} catalyst without losing too much transparency. Tricyclononene (TCN) monomers are proposed to be one solution. Trifluoro-TCN and pentafluoro-TCN homopolymers were prepared and show improved transparency. Functional NBHFOH and CF_3TCN copolymers were successfully prepared. For the NBHFOH/CF_3TCN copolymer (83/17), the absorbance is 1.67 μm^{-1} at 157 nm and for 74/26 copolymer it is 1.97 μm^{-1}.

Another Alicyclic polymer platform: NorBornene HexaFluoroalcOH (NBHFOH)-*co*-t-BOC platform

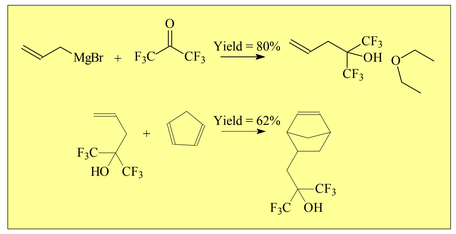
NBHFOH-*co*-TCN platfrom (Please see TCN poster)

NorBornene HexaFluoroalcOH (NBHFOH)-*co*-t-BOC platform

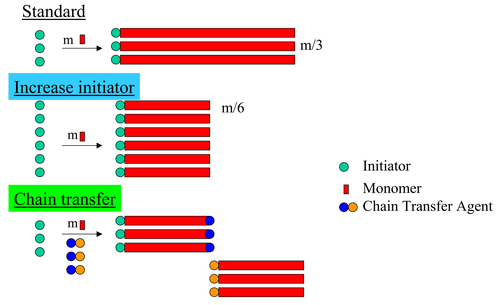


- Excellent optical transparency
- Poor contrast
  -High molecular weight → Swelling

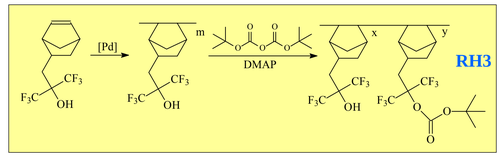
Synthesis of Bicyclo[2.2.1]hept-5-ene-2-(1,1,1-trifluoro-2-trifluoromethylpropan-2-ol)



Reduction of MW

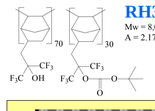


Improvement Plan



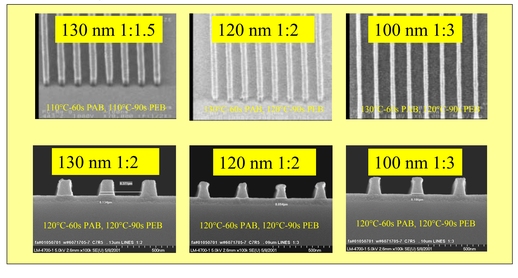
Increase the catalyst loading
↓
Lower the molecular weight
↓
Acceptable images

Imaging Results



RH3
Mw = 8,000
A = 2.17 μm^{-1}

Formulation:
RH3,6wt% TPS-Nf, 0.3wt% TBAH in PGMEA
Conditions:
157 nm exposure (0.6NA-0.7σ, 17.3 mJ/cm²), binary mask, 160 nm thick resist on 82 nm anti-reflective layer (G0), 20 sec 0.26N TMAH development



Conclusion:

This platform looks promising. Its has excellent optical transparency, we propose to print images with higher aspect ratios. This material is very new. We are still exploring the optimal polymer composition ratio and the process conditions for sub-100 nm features.

The authors gratefully acknowledge International SEMATECH and its member companies for the support of this project. Dr. Ralph Dammel from AZ Clariant and Central Glass Co. are also acknowledged for their generous donation of key monomers. Will Conley, Danny Miller, Shashikant Patel, Hoang Vi Tran, Dr. Scott MacDonald for their imaging efforts. We are indebted to JSR Corporation for support of Mr. Takashi Chiba and Eternal Co. for support of Dr. Yu Tsai Hsieh. Finally, we acknowledge the help of our undergraduate, Anthony Vander Heyden.