Radical Polymerization for 157 nm Resists

Charles R. Chambers Jr.

The University of Texas at Austin

9/11/2001



COMA polymers for 193nm applications



- Can analogous alternating polymers be made from monomers that are transparent at 157nm?
- Note that the introduction of fluorine on norbornene reduces electron density.... We need very electron deficient co-monomers

Some Successful Radical Copolymerizations



Many others were tested but did not produce polymer

Free Radical Co-polymerizations

- Focus will now be on Characterization
 - Purification
 - Classical Chemical characterization
 - Spectral Properties
 - VASE Measurements

Preliminary results look promising for cyanoacrylate and α -trifluoromethyl acrylate co-polymers

- Thermal analysis
 - TGA
 - DSC



Radical polymerization of norbornene



tert-Butyl Peroxide Initiation for 193nm



We also tested :

- benzoyl peroxide
- Hydrogen peroxide
- AIBN

Okoroanyanwu, U. Ph.D. Thesis, University of Texas at Austin, 1997.

Cho, S. Ph.D. Thesis, University of Texas at Austin, 2000.

Dr. Cho's Data

Initial -COOH Content (Mole%!!)	Yield	Polymer -COOH content (Mole %)	M.W.
5	8%	10	26,400
10	19%	12	30,000
15	48%	13	47,300
25	38%	17	49,900
35	35%	30	51,800
50	51%	39	9,300
70	54%	51	7,100

Cho, S. Ph.D. Thesis, University of Texas at Austin, 2000.



Application to 157nm

Geminally substituted monomers undergo radical initiated polymerization with Di-t-butyl peroxide

Homopolymers

Copolymers





Radical initiation does not yet provide polymers that are as "clean" as the metal catalyzed process



Highest yield requires an equivalent of peroxide initiator!!

Mole% Initiator	%Yield	Mw
20	15	2,530
80	47	2,900
160	32	3,260

This is Dangerous !!



If you try this, please use Caution!!

But....the polymers function effectively



Free Radical Polymerization Summary

- The advantages
 - Low metal contamination
 - "Ease" of synthesis
- We can now make are several interesting "regular" copolymers
 - More by Brian Trinque
- Homopolymerization of geminally substituted norbornene is possible
 - Higher absorbance (to date)
 - Extremely high initiator ratios are required (danger)
 - Polymers are imageable at 157nm



Future Work

- Continue to audition co-monomers
 - Difluoromaleic anhydride, etc.
- Careful characterization of current samples
- Study mechanism of polymerization
- Collaboration with Dr. Dixon at PNNL
 - Calculate Q and e values
 - Estimate activation bariers

Acknowledgements **Raymond Hung** Yu-Tsai Hsieh (Eternal Company) Vanessa Dimas (SRC Summer Fellow) Brian Osborn **Brian Trinque Thomas Mrozek SEMATECH**

