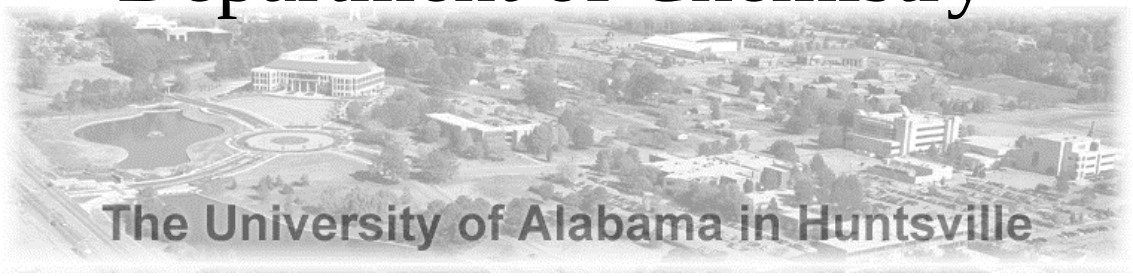
Surface Modification of Polymer Substrates by Excimer Radiation

Emanuel Waddell

Department of Chemistry

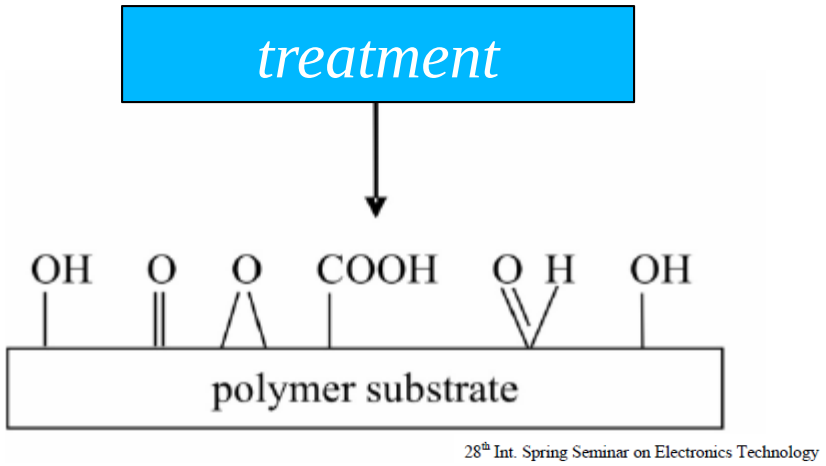


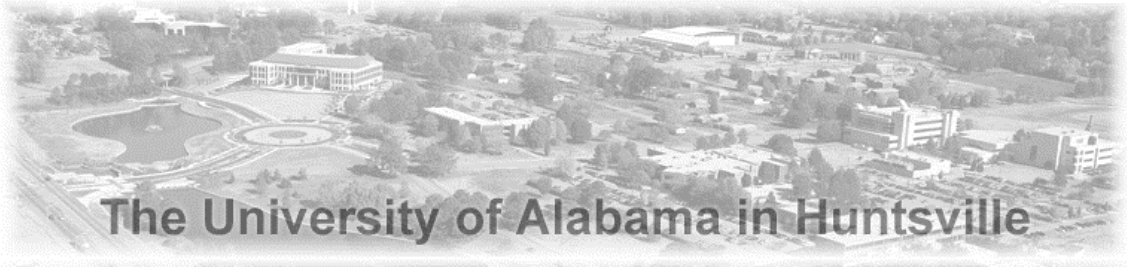
Surface Modification

biocompatibility – metallization - wettability

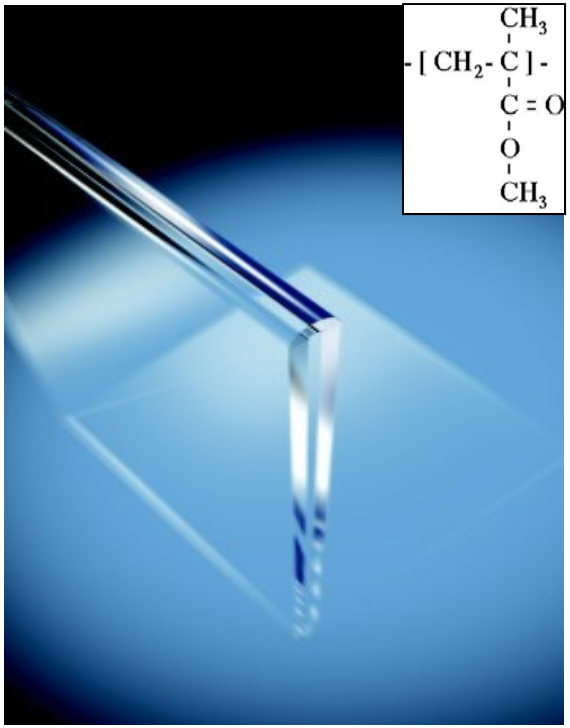
tensile strength-elasticity-color-clarity
tear strength-hardness-impact strength

Wet chemical treatments
Plasma treatments
Photochemical treatments
Mechanical roughening
Corona Discharge
Ion Implantation





# of Polymer Substrates



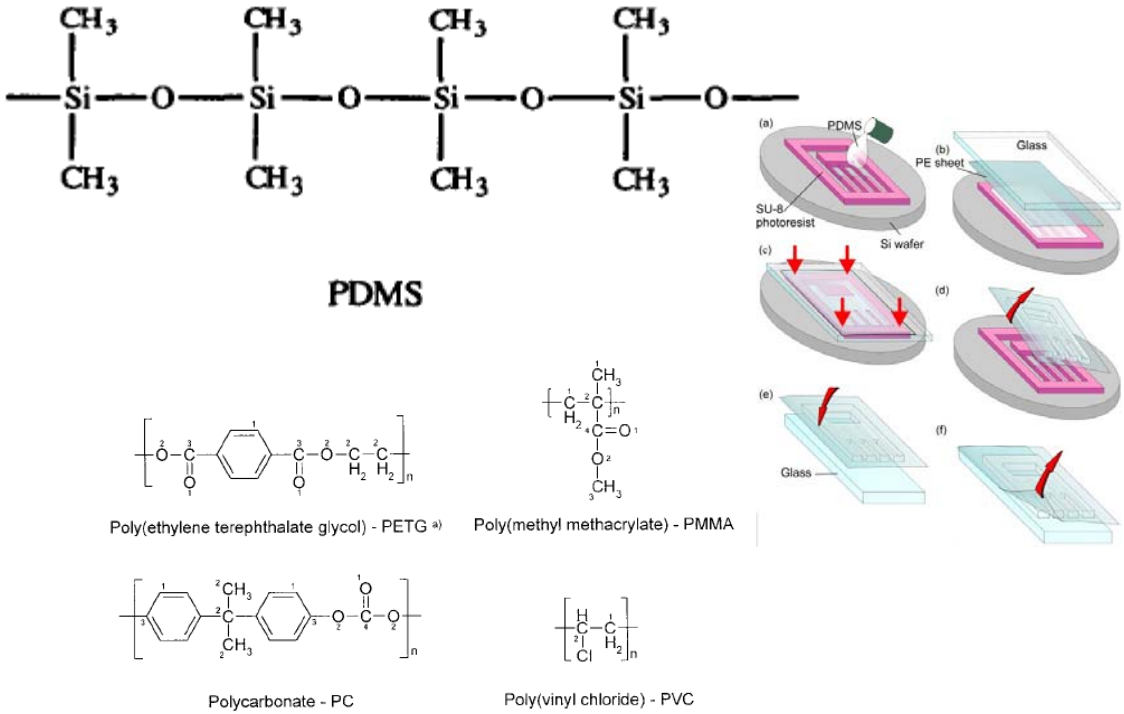
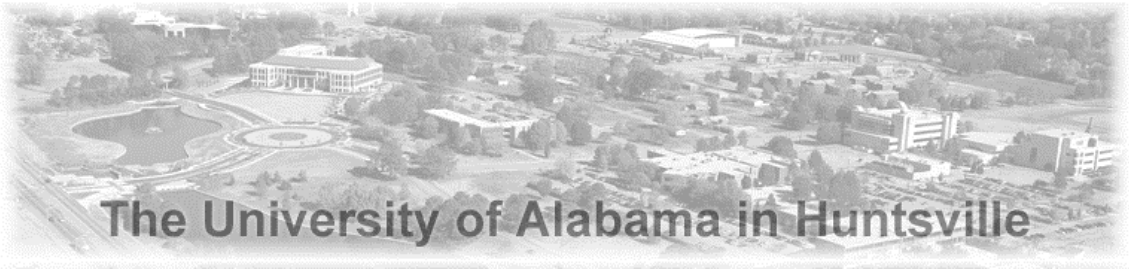
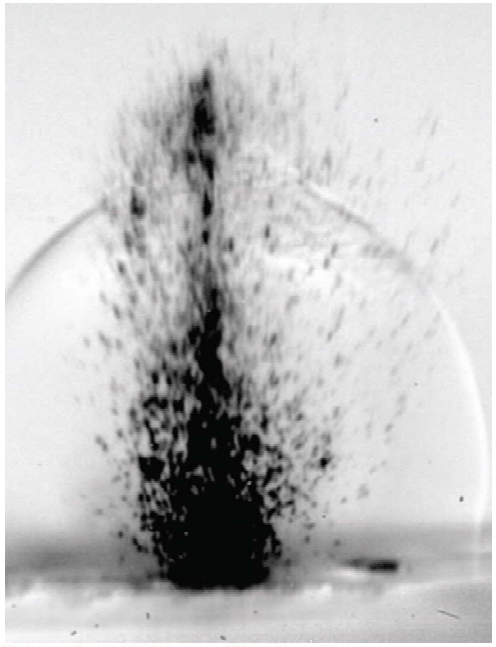
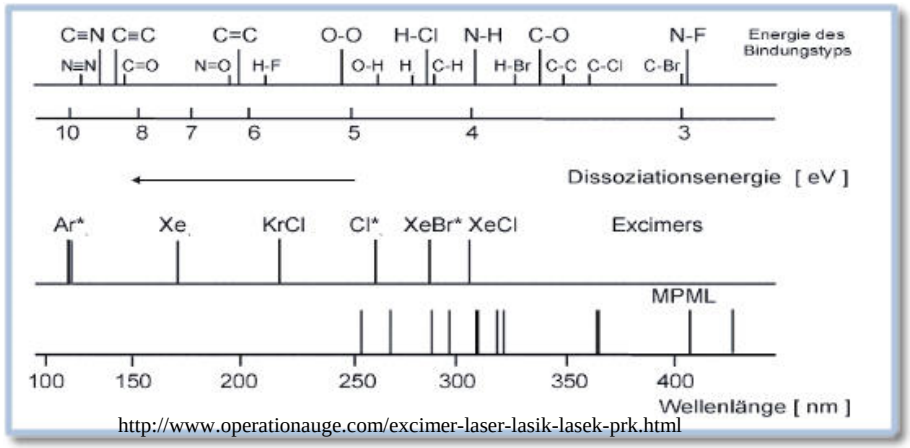


Figure 1. Chemical structures of polymers investigated in the present study. a)Monomer structure of the major component of PETG. See text.



by Excimer Radiation





http://www.operationauge.com/excimer-laser-lasik-lasek-prk.html

Interaction of Photons with Polymers:
From Surface Modification to Ablation

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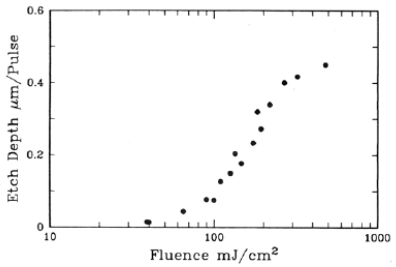

Figure 2. Plot of etch depth vs log (fluence) in laser ablation of PMMA at 193 nm.

Chemical Reviews, 1989, Vol. 89, No. 6

A new and emerging technology: Laser-induced surface modification of polymers

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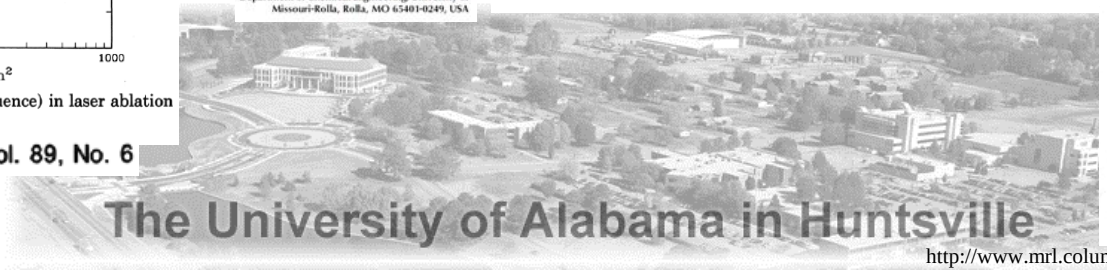
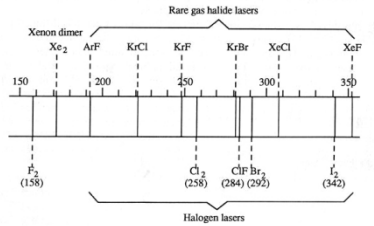
Box 1. Unique characteristics of laser light

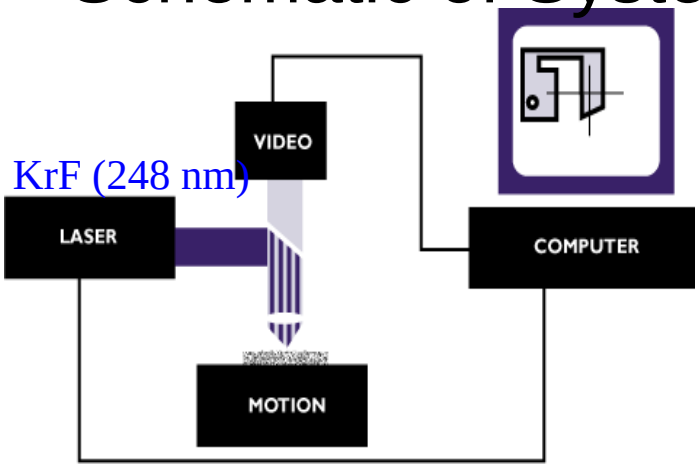
- It is coherent. This means that it is highly organized and, therefore, laser beams stay together (in phase) over relatively long distances and long periods of time.
- It is intense. This means that laser energy is concentrated.
- It is directional or highly collimated. This means that it can travel over long distances while maintaining its energy concentration. Therefore, laser beams can be directed efficiently on to almost any location even from long distances without any energy being lost.
- It is monochromatic. This means that it is highly single-colored. Therefore, it can be used to interact selectively with various materials including metals, plastics, paper, glass, etc.
- It has great focusability. This means that laser light can be focused to smaller spots, which provide higher photon fluxes in small volumes, depending on the available power.
- It may be in a continuous wave or pulsed mode of operation. This means that laser light energy can be generated in a continuous or non-continuous fashion allowing a wide range of materials to be treated successfully.
- It is not subject to wear and tear. This means that contamination of material being processed is avoided.
- It is easily, efficiently and reliably manipulated and controlled, providing constant processing characteristics, great confidence and precision in any application.





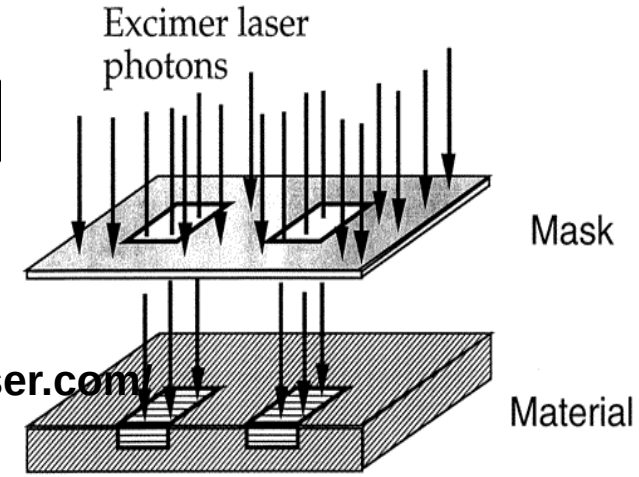
http://www.mrl.columbia.edu/ntm/level1/ch05/html/l1c05s05.html

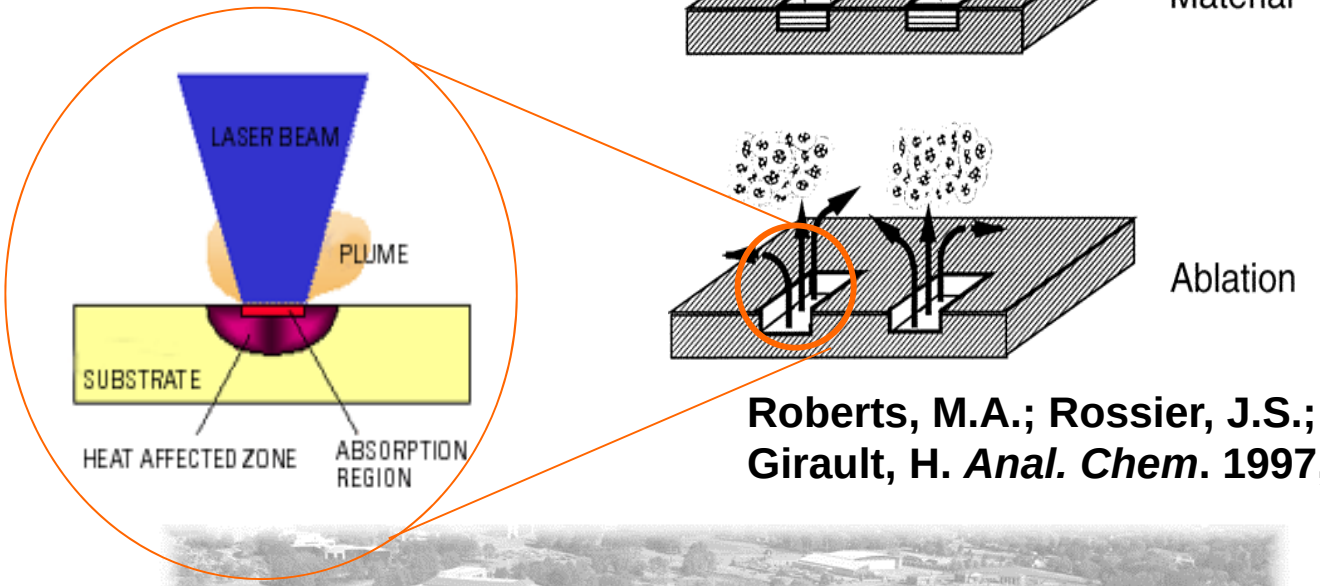
Schematic of System



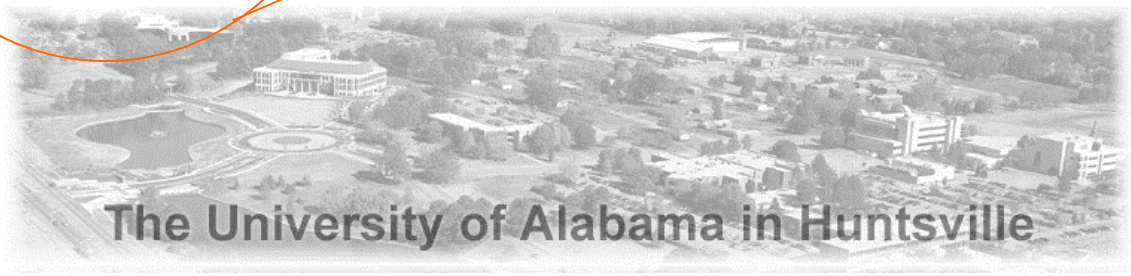
http://potomac-laser.com/

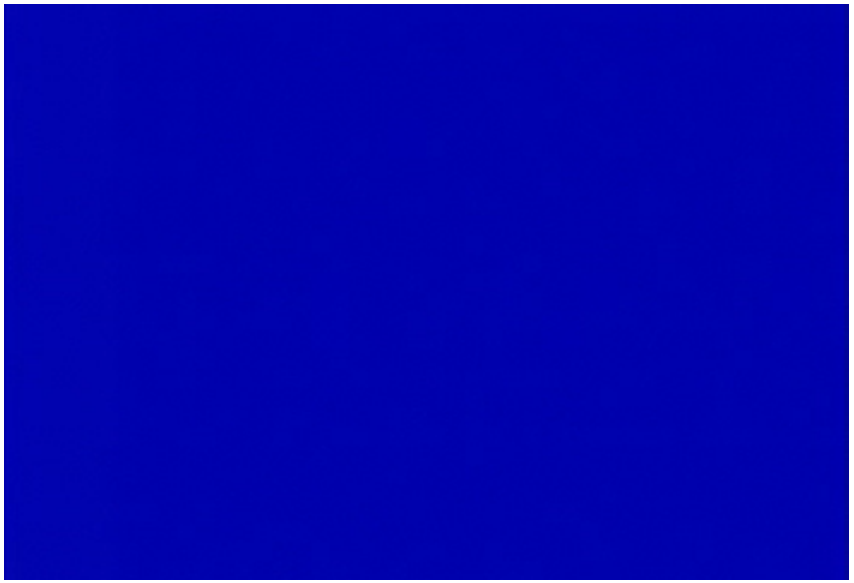
Ablation Process

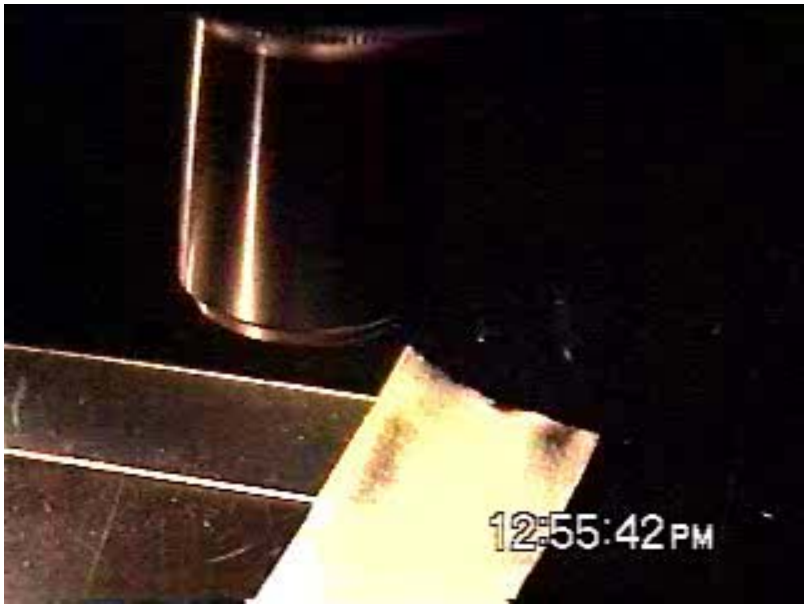


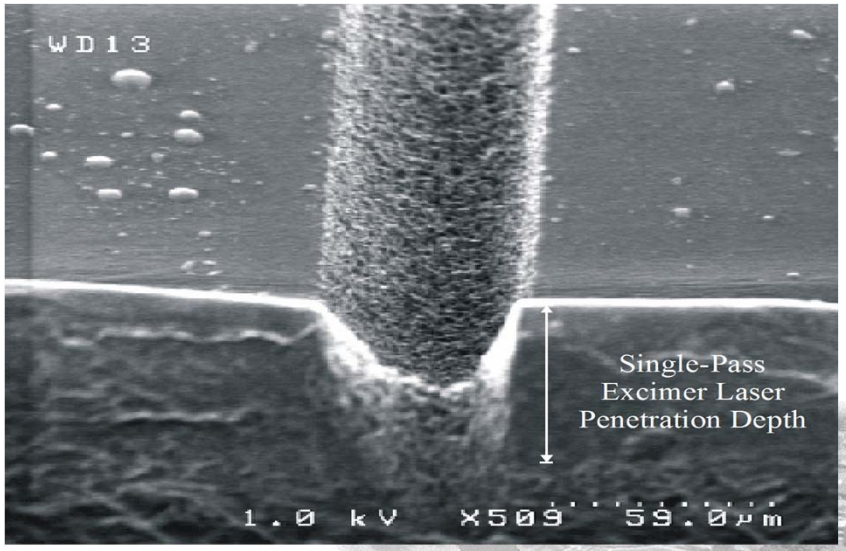


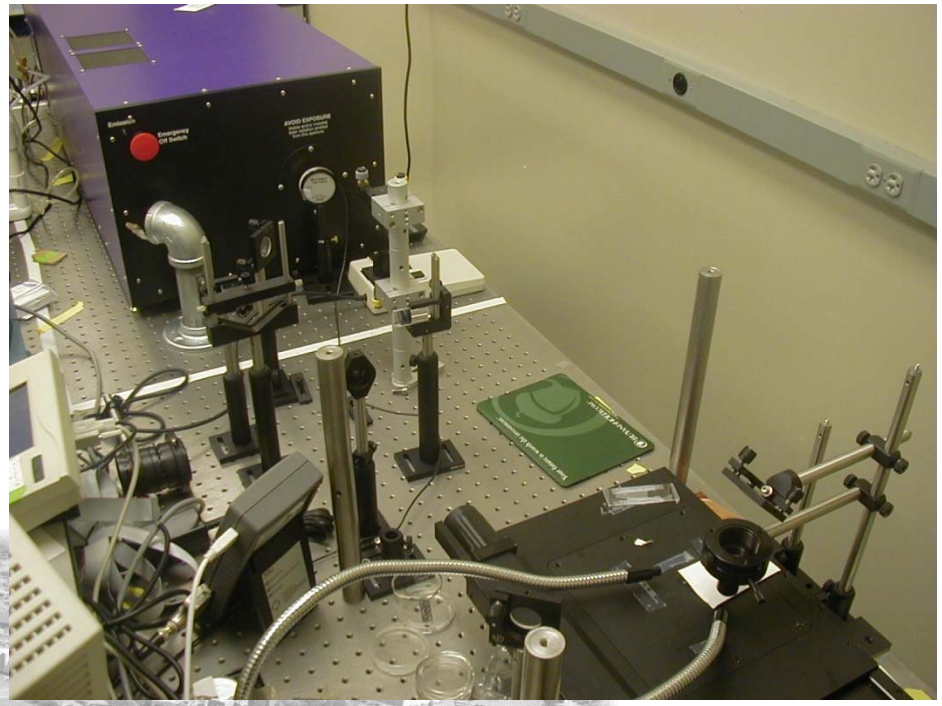
Roberts, M.A.; Rossier, J.S.; Bercier, P.; and Girault, H. *Anal. Chem*. 1997, *69*, 2035-2042

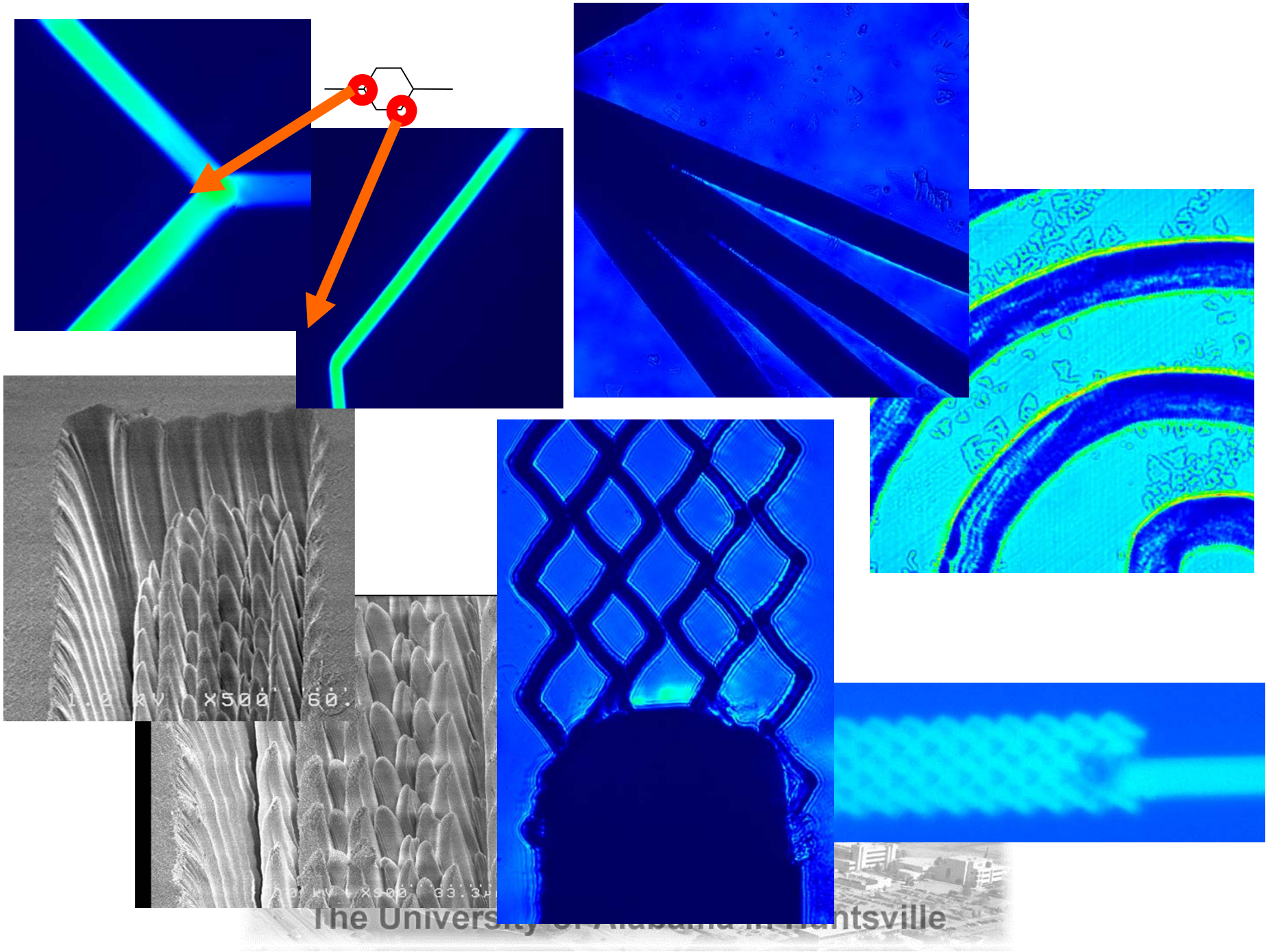




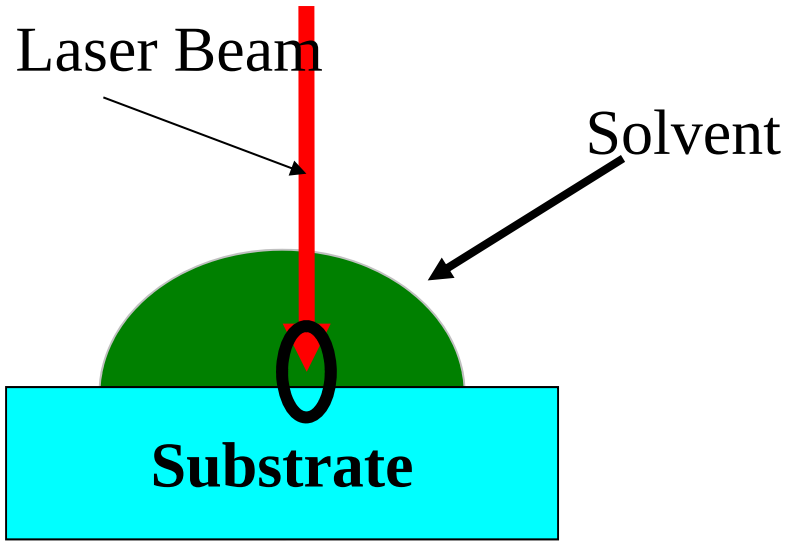

12:55:42 PM

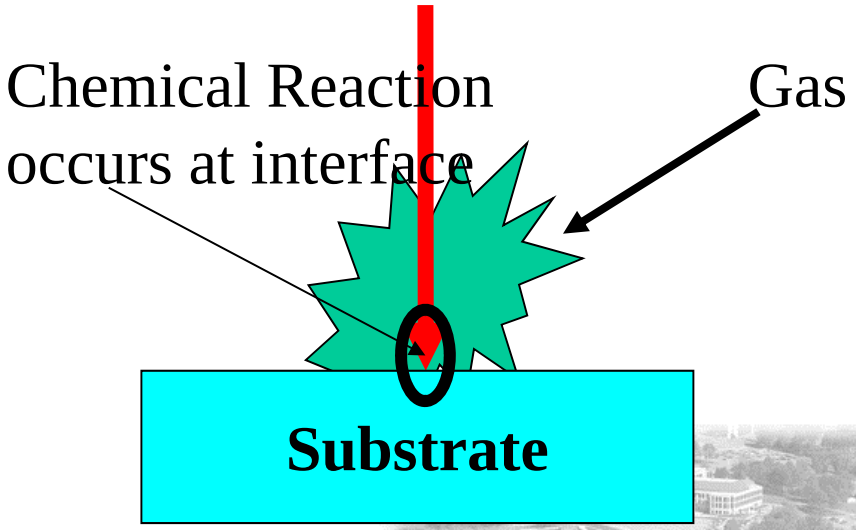

WD13
Single-Pass
Excimer Laser
Penetration Depth
1.0 kV X509 59.0µm

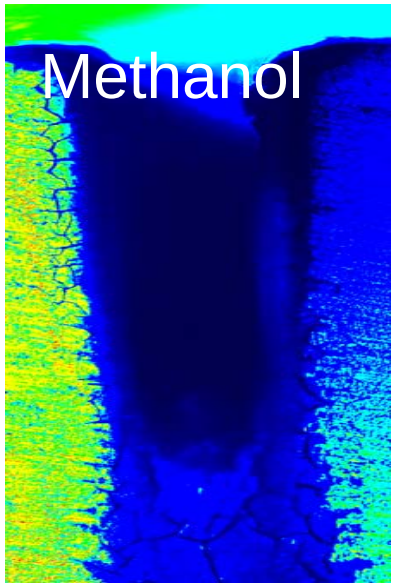


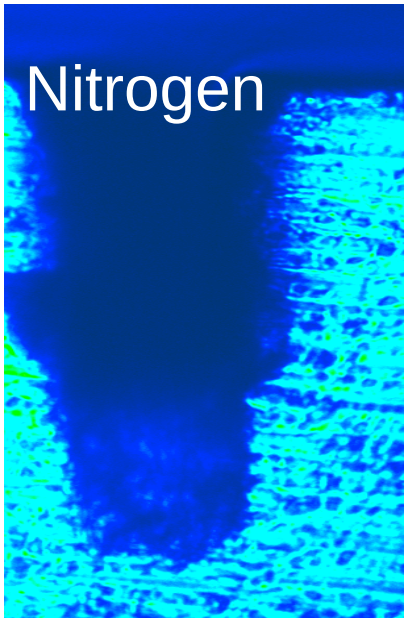

The University of Alabama in Huntsville

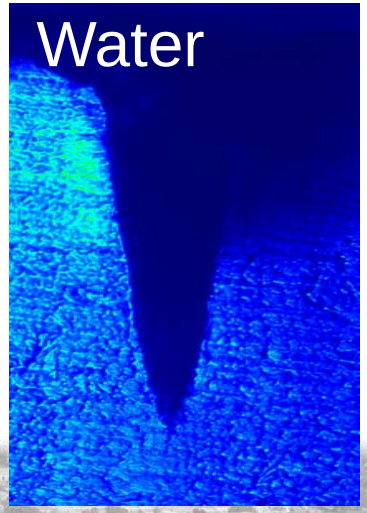
Ablation under Different Atmospheres

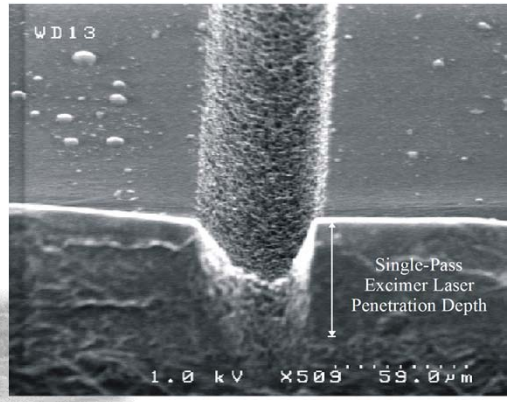


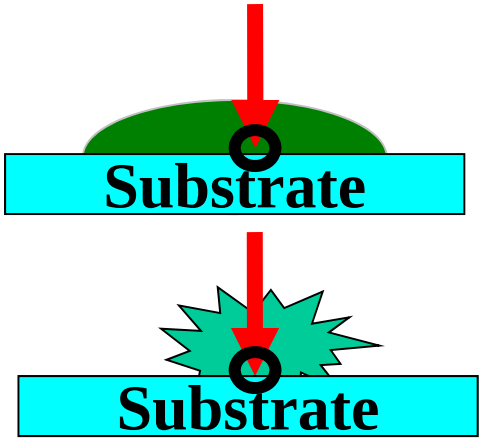


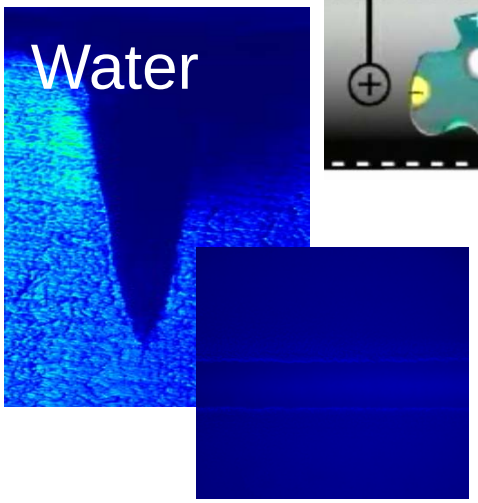


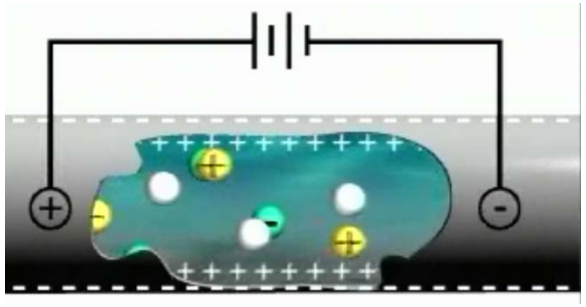




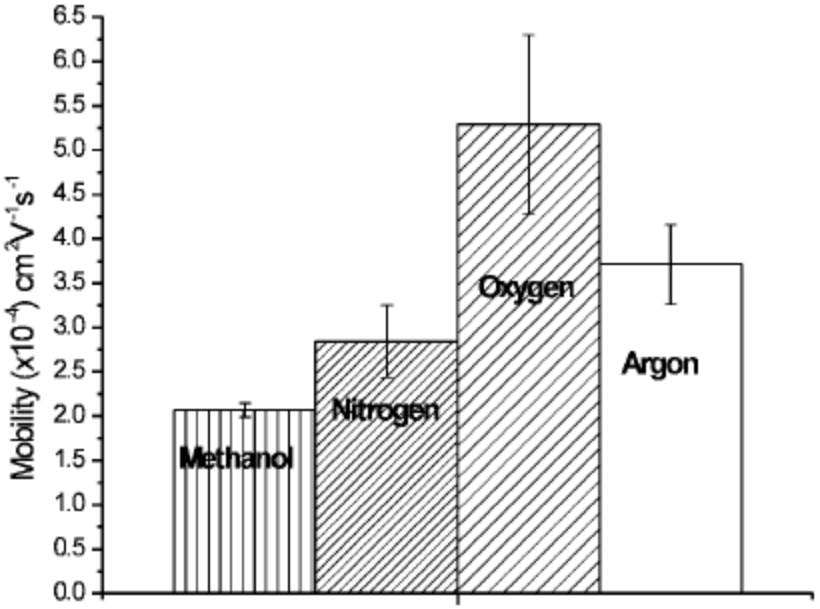


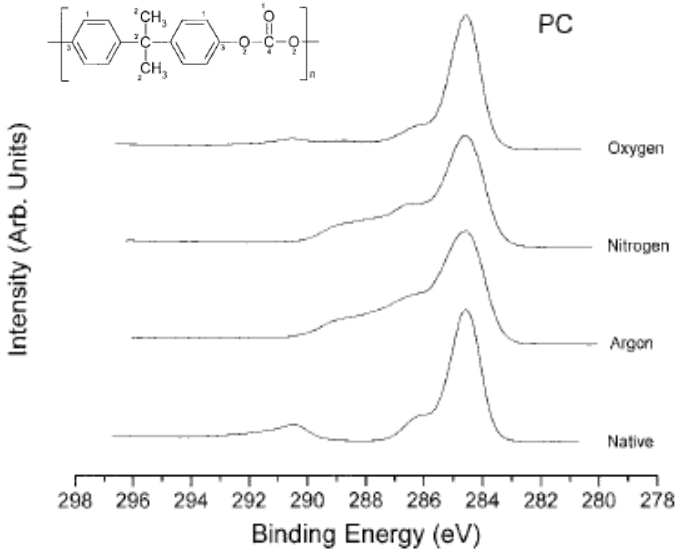






	native	argon	nitrogen	oxygen	expected[a]
O/C	0.19	0.39	0.40	0.26	0.19
COOX/C	0.09	0.12	0.13	0.06	0.06
EO mobility	na	3.71 ± 0.45[c]	2.84 ± 0.41[c]	5.29 ± 1.01[c]	na





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Surface Characterization of Laser-Ablated Polymers Used for Microfluidics

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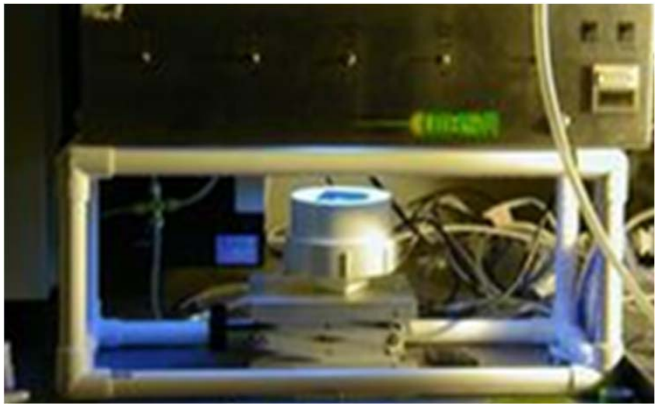
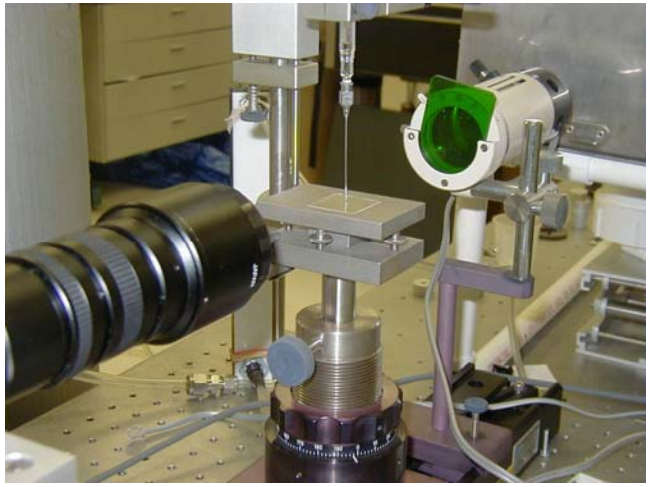
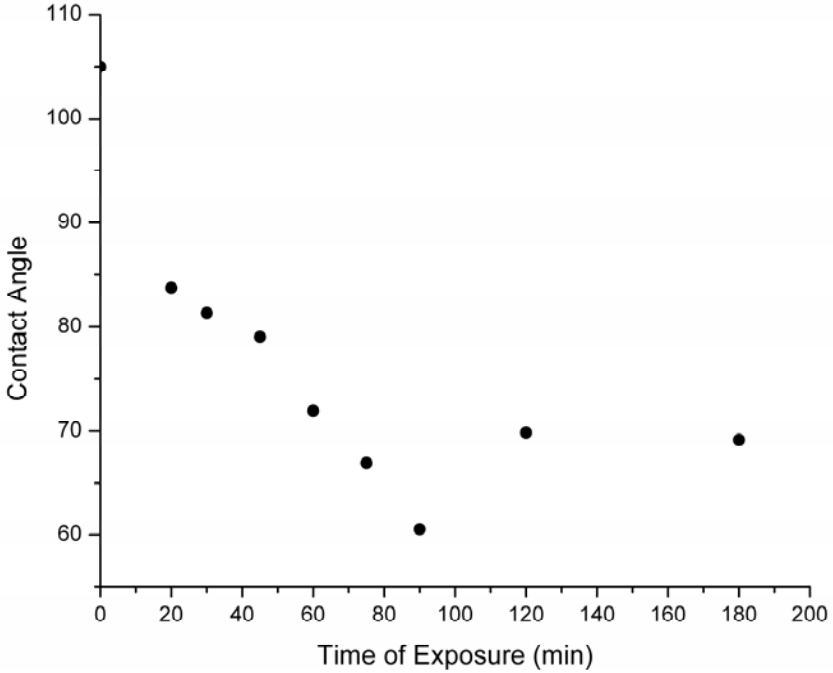
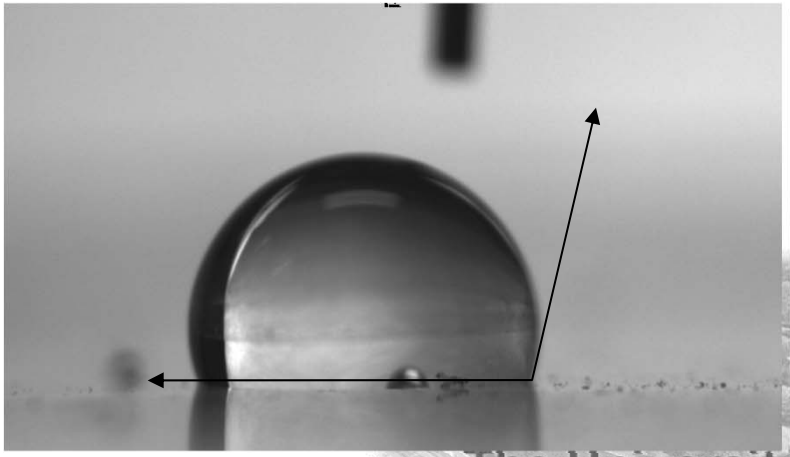
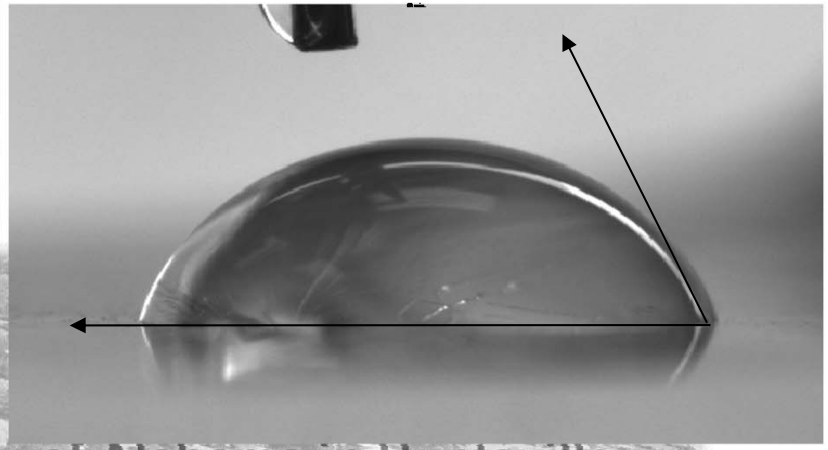
National Institute of Standards and Technology, Gaithersburg, Maryland 20899, and Center for Microanalysis of Materials, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

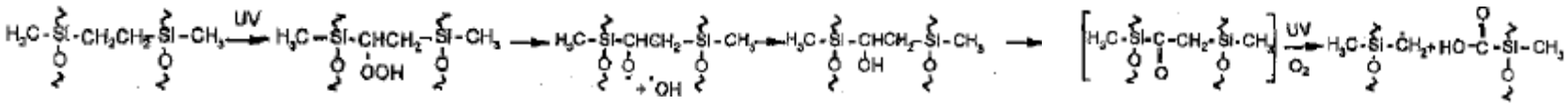





Contact Angle
110
100
90
80
70
60
0
20
40
60
80
100
120
140
160
180
200
Time of Exposure (min)

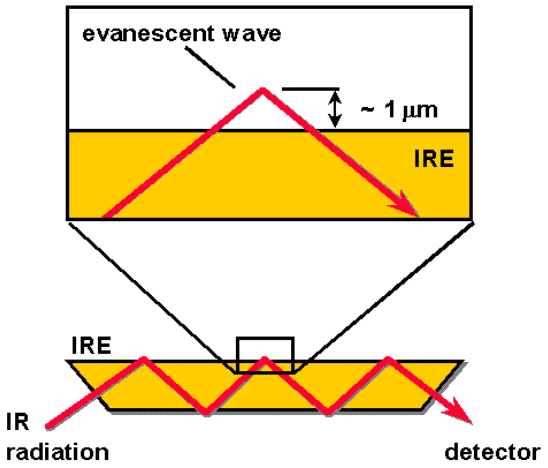


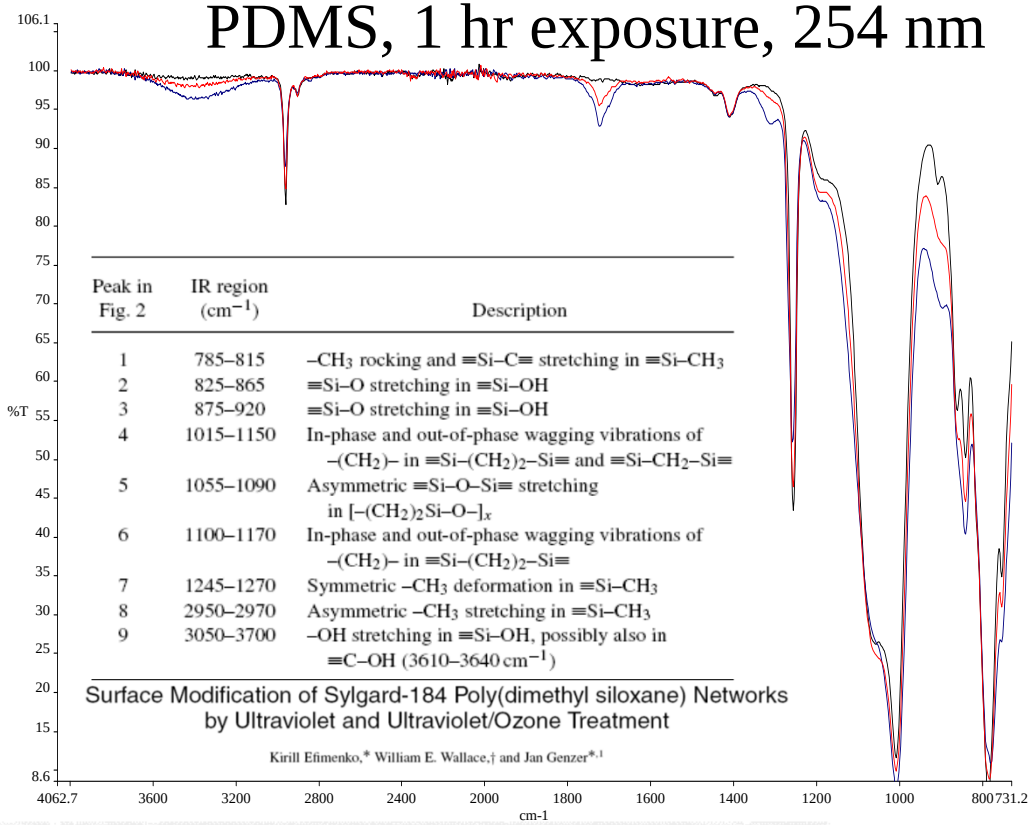




"Hydrophobicity Changes in Silicone Rubbers"; Hillborg and Gedde, IEEE Trans. In Diel. And Elect. Insulation 6 (5) 1999

PDMS, 1 hr exposure, 254 nm

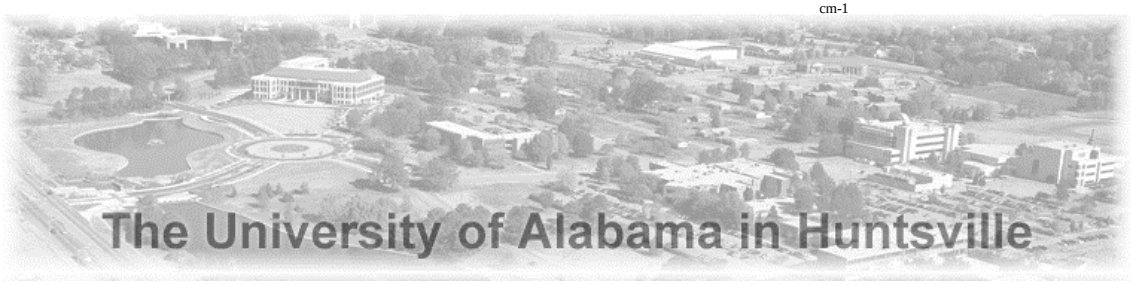




Peak in Fig. 2	IR region (cm^{-1})	Description
1	785–815	$-CH_3$ rocking and $\equiv Si-C\equiv$ stretching in $\equiv Si-CH_3$
2	825–865	$\equiv Si-O$ stretching in $\equiv Si-OH$
3	875–920	$\equiv Si-O$ stretching in $\equiv Si-OH$
4	1015–1150	In-phase and out-of-phase wagging vibrations of $-(CH_2)-$ in $\equiv Si-(CH_2)_2-Si\equiv$ and $\equiv Si-CH_2-Si\equiv$
5	1055–1090	Asymmetric $\equiv Si-O-Si\equiv$ stretching in $[-(CH_2)_2Si-O-]_x$
6	1100–1170	In-phase and out-of-phase wagging vibrations of $-(CH_2)-$ in $\equiv Si-(CH_2)_2-Si\equiv$
7	1245–1270	Symmetric $-CH_3$ deformation in $\equiv Si-CH_3$
8	2950–2970	Asymmetric $-CH_3$ stretching in $\equiv Si-CH_3$
9	3050–3700	$-OH$ stretching in $\equiv Si-OH$, possibly also in $\equiv C-OH$ (3610–3640 cm^{-1})

Surface Modification of Sylgard-184 Poly(dimethyl siloxane) Networks by Ultraviolet and Ultraviolet/Ozone Treatment

Kirill Efimenko,* William E. Wallace,† and Jan Genzer*,‡



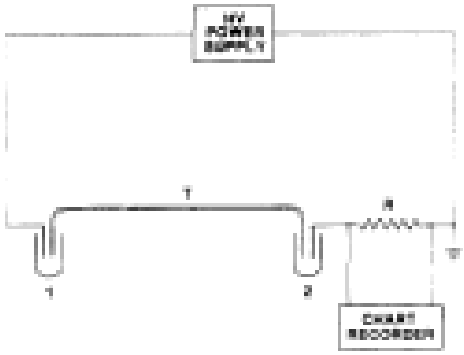


Figure 1. Schematic diagram of the current measurement for determining the electroosmotic flow rate. Here 1 and 2 denote electrolyte reservoirs, which are connected by the capillary tube T.

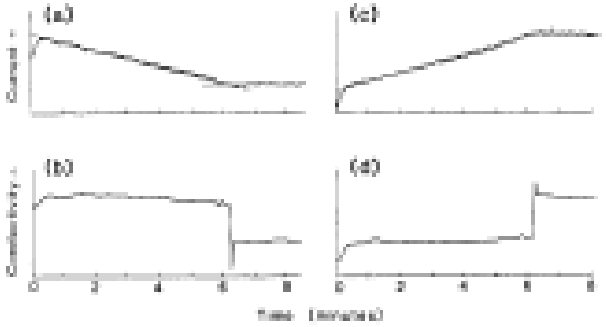
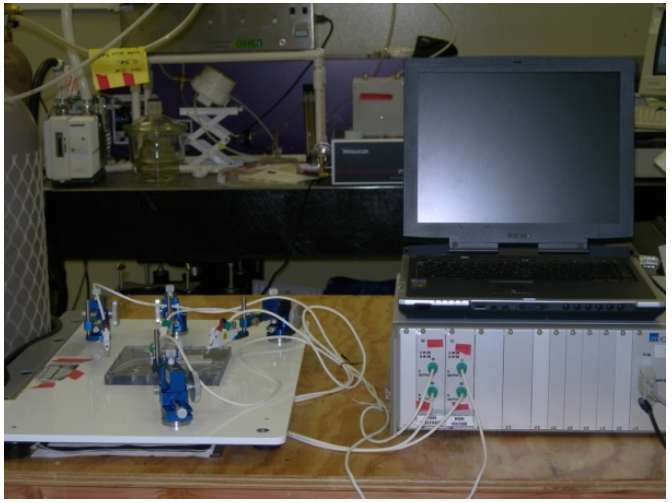
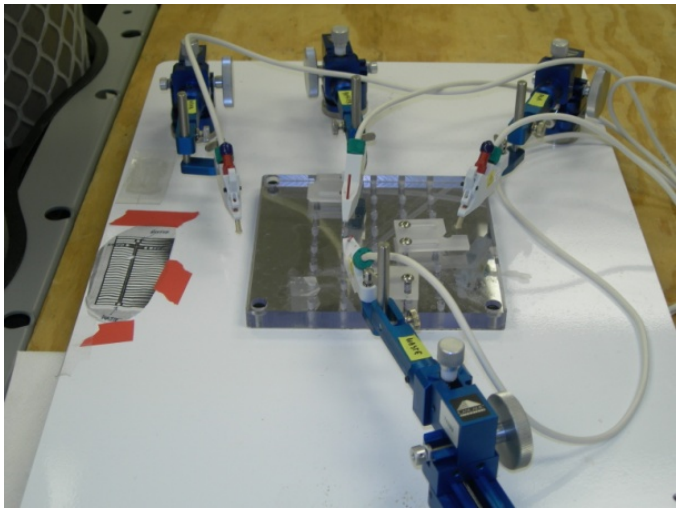


Figure 2. Electropherograms showing the measurement of the electroosmotic flow rate. Trace a shows the CZE current versus time for 18 mM phosphate buffer replacing 20 mM phosphate buffer in the capillary tube, and trace b shows, under the same conditions, the conductivity change. Traces c and d are the corresponding electropherograms when 20 mM phosphate buffer replaces 18 mM phosphate buffer in the capillary tube. The actual operating conditions are given in the text. In traces a and c regression lines are indicated to aid identification of the slope change.

Anal. Chem. **1988**, *60*, 1837–1838

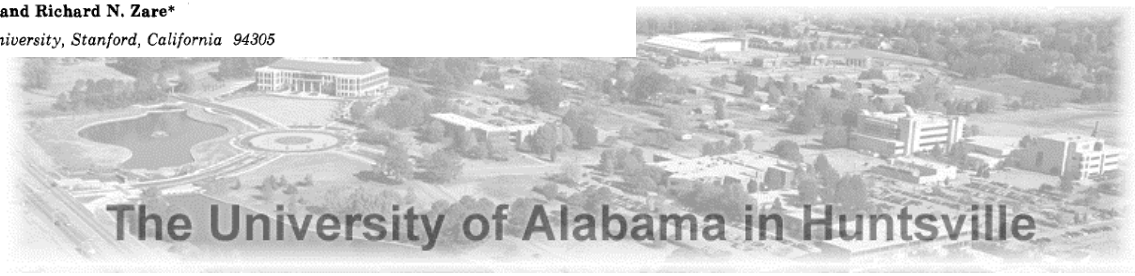


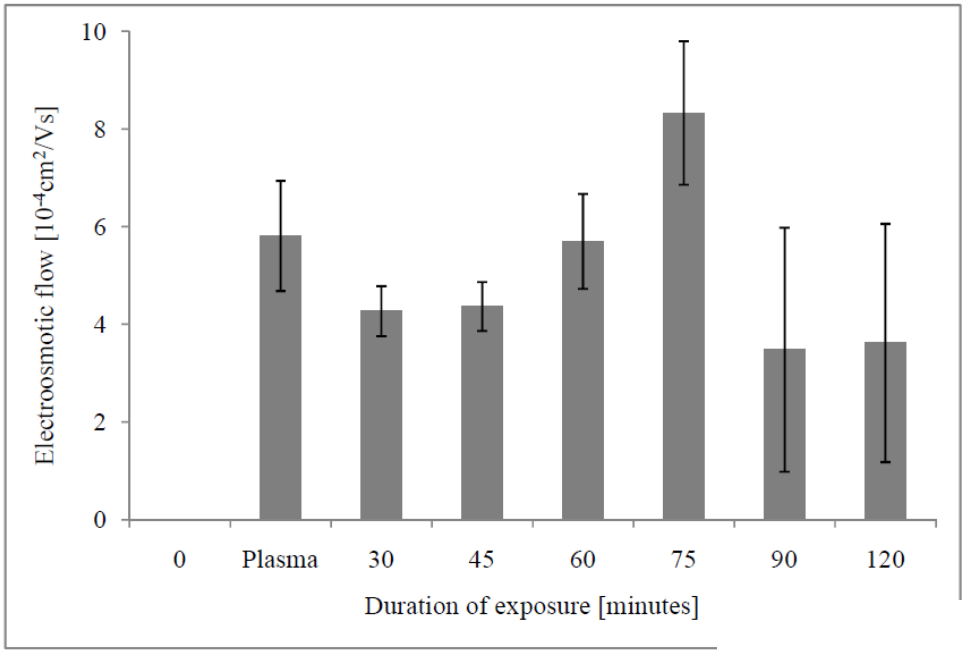


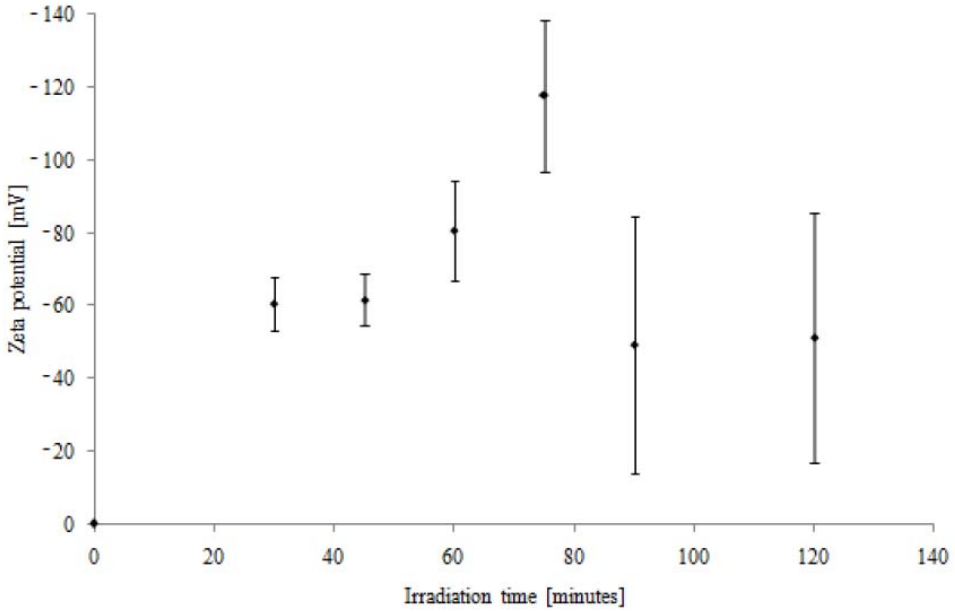
Current-Monitoring Method for Measuring the Electroosmotic Flow Rate in Capillary Zone Electrophoresis

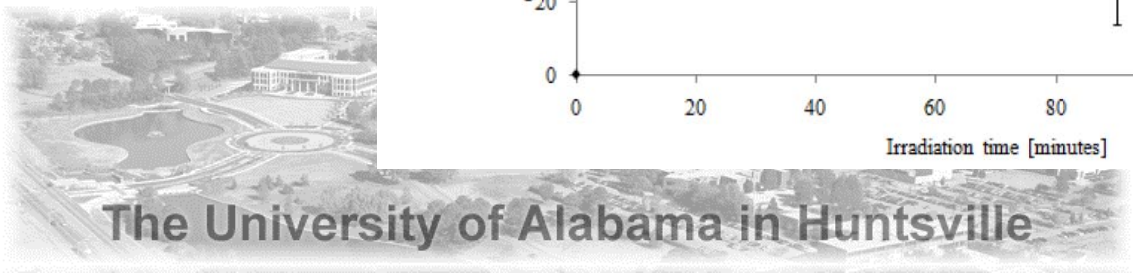
Xiaohua Huang, Manuel J. Gordon, and Richard N. Zare*

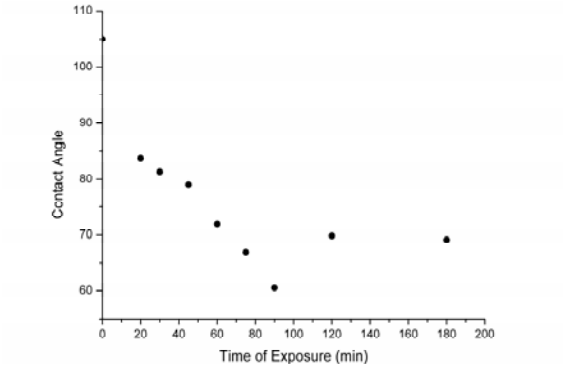
Department of Chemistry, Stanford University, Stanford, California 94305

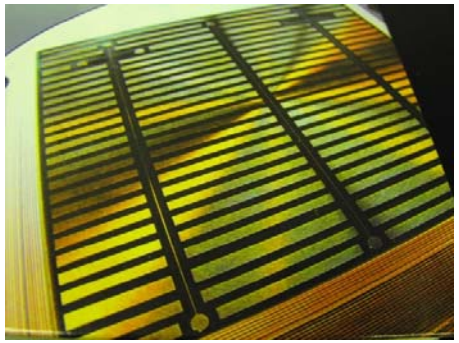


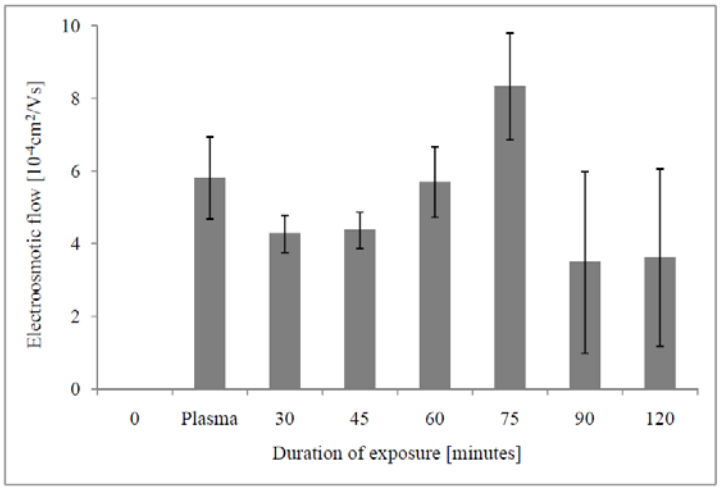

Electroosmotic flow [10-4cm2/Vs]
10
8
6
4
2
0
0
Plasma
30
45
60
75
90
120
Duration of exposure [minutes]


Zeta potential [mV]
-140
-120
-100
-80
-60
-40
-20
0
0
20
40
60
80
100
120
140
Irradiation time [minutes]

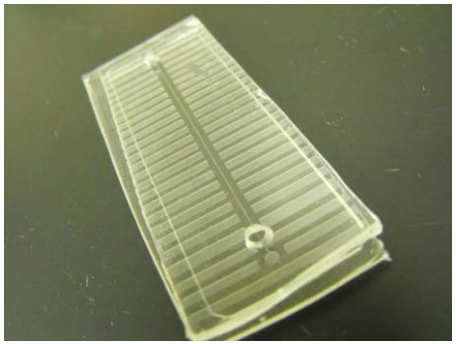

The University of Alabama in Huntsville

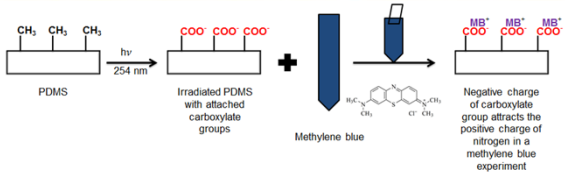

Contact Angle
Time of Exposure (min)

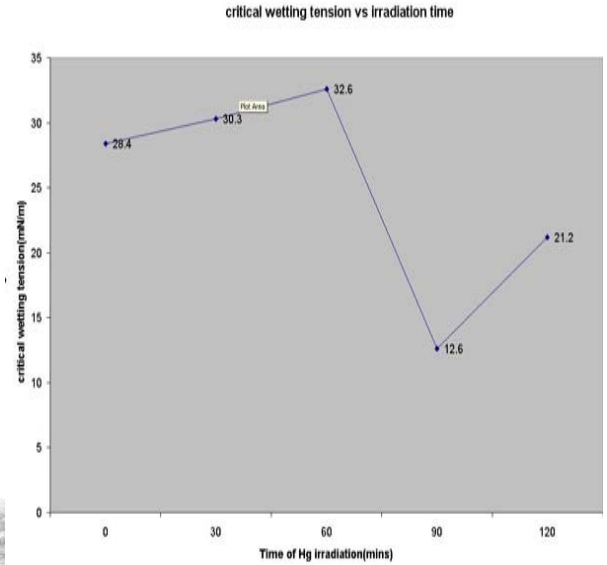


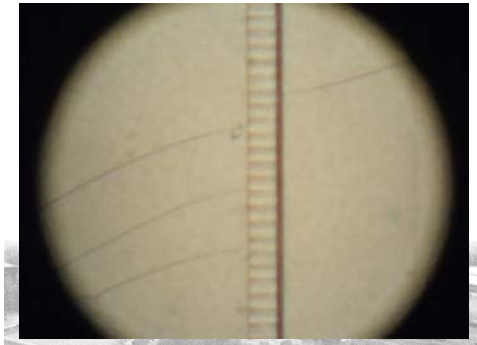

Electroosmotic flow [10⁻⁴cm²/Vs]
0
Plasma
30
45
60
75
90
120
Duration of exposure [minutes]

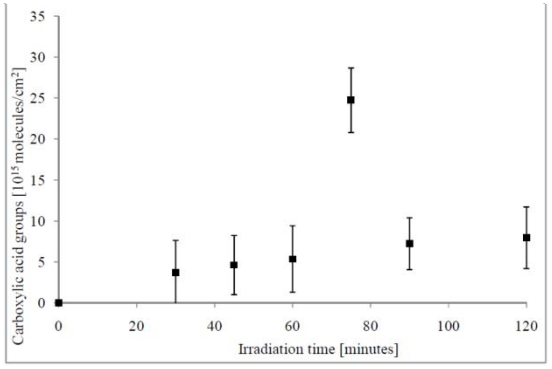

0
30
45
60
75
90
120

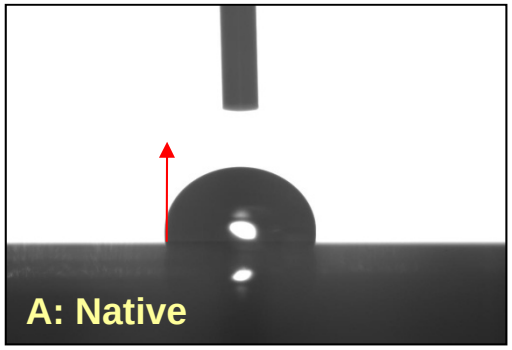


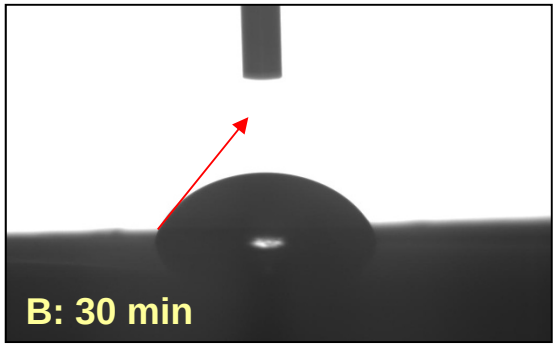

PDMS
hν
254 nm
Irradiated PDMS with attached carboxylate groups
Methylene blue
Negative charge of carboxylate group attracts the positive charge of nitrogen in a methylene blue experiment

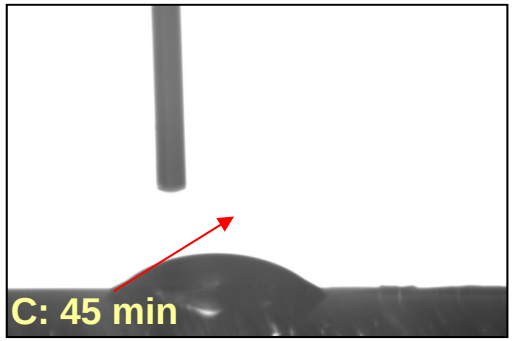

critical wetting tension vs irradiation time
critical wetting tension(mN/m)
28.4
30.3
32.6
12.6
21.2
Time of Hg irradiation(mins)

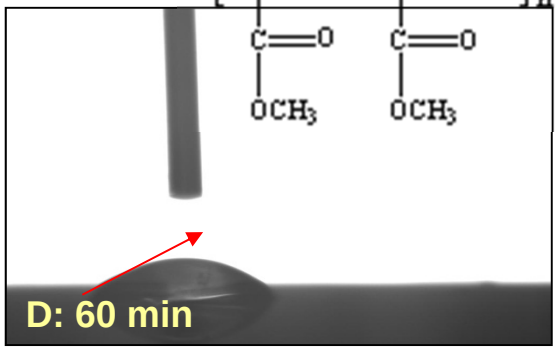



Carboxylic acid groups [10¹⁵ molecules/cm²]
Irradiation time [minutes]

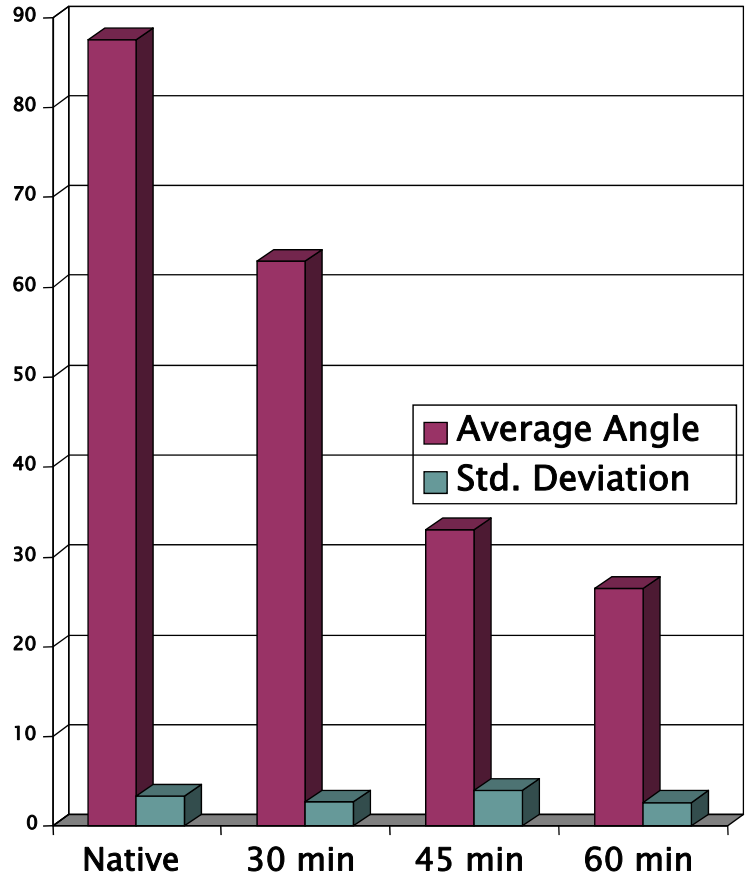

A: Native

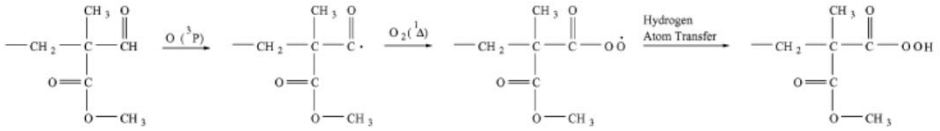

B: 30 min

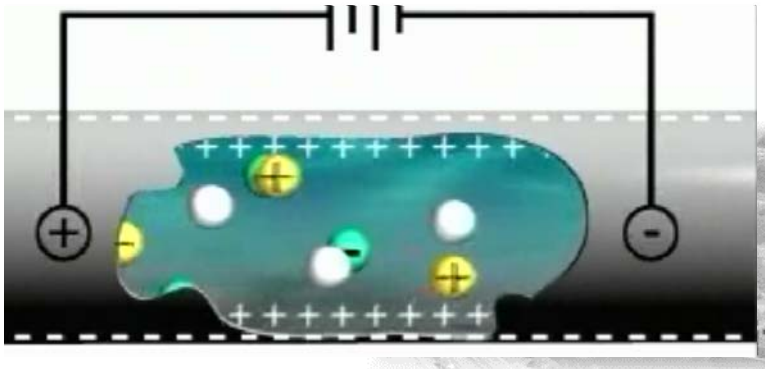

C: 45 min

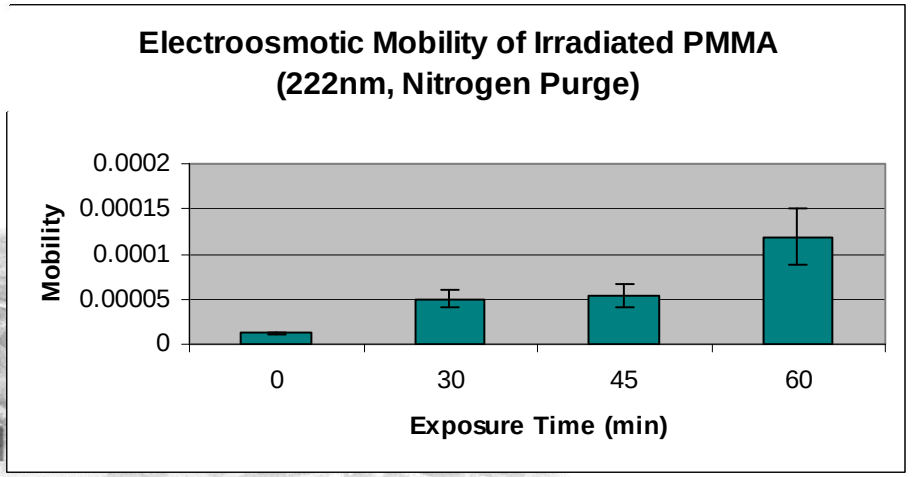

D: 60 min

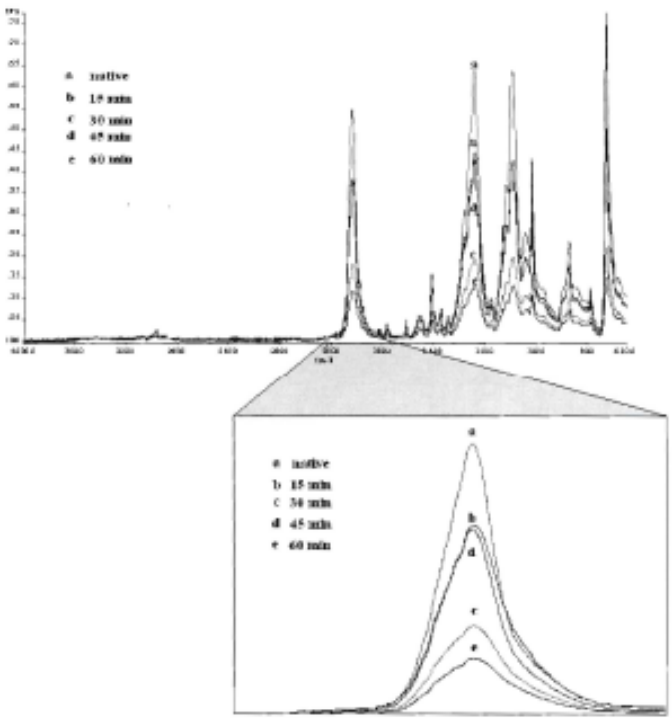
CH3
CH3
C—CH2—C—CH2
n
C=O
C=O
OCH3
OCH3

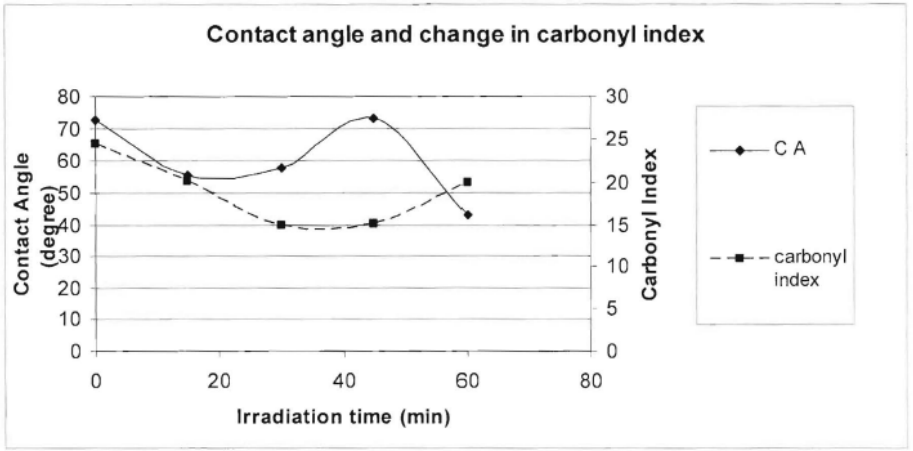

90
80
70
60
50
40
30
20
10
0
Average Angle
Std. Deviation
Native
30 min
45 min
60 min

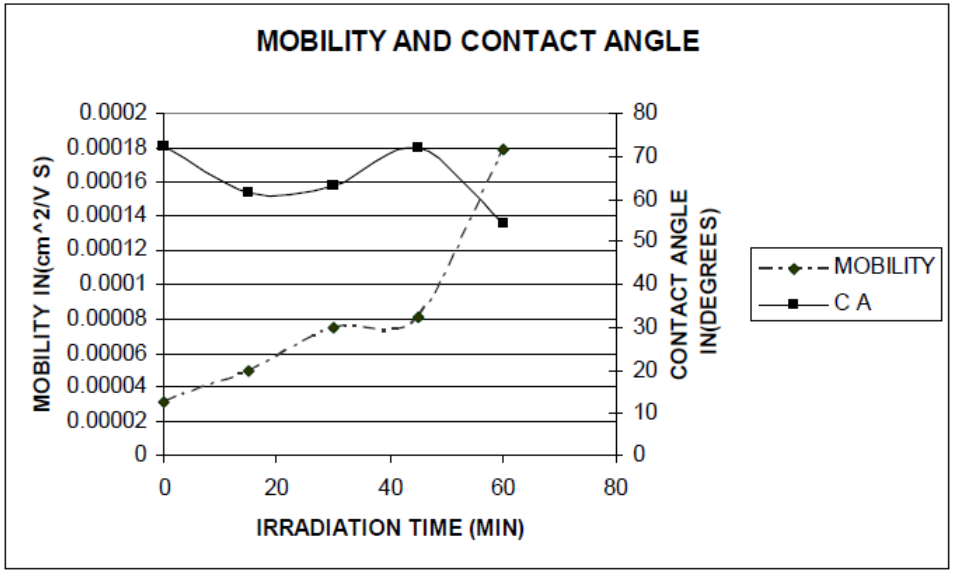

O (3P)
O2(1Δ)
Hydrogen
Atom Transfer
OOH

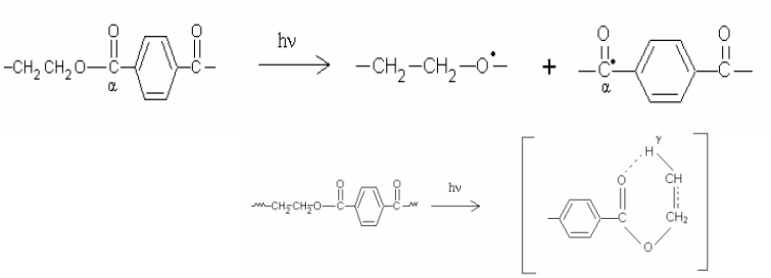



Electroosmotic Mobility of Irradiated PMMA
(222nm, Nitrogen Purge)
Mobility
0.0002
0.00015
0.0001
0.00005
0
0
30
45
60
Exposure Time (min)

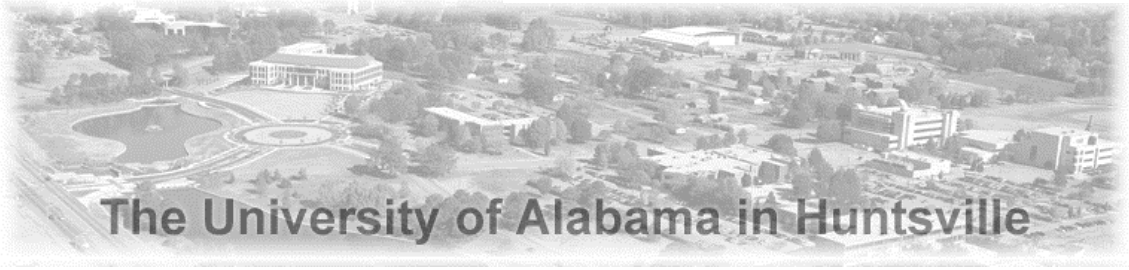

a native
b 15 min
c 30 min
d 45 min
e 60 min


Contact angle and change in carbonyl index
Contact Angle (degree)
Carbonyl Index
Irradiation time (min)
C A
carbonyl index


MOBILITY AND CONTACT ANGLE
MOBILITY IN(cm^2/V S)
CONTACT ANGLE IN(DEGREES)
IRRADIATION TIME (MIN)
MOBILITY
C A


hν

hν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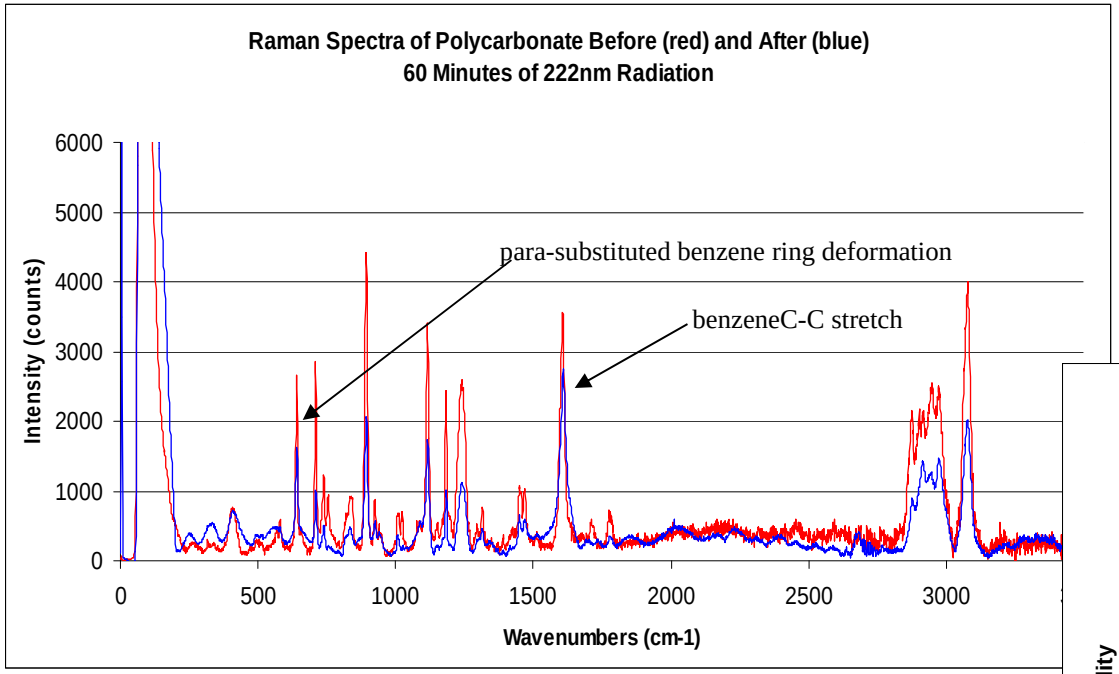
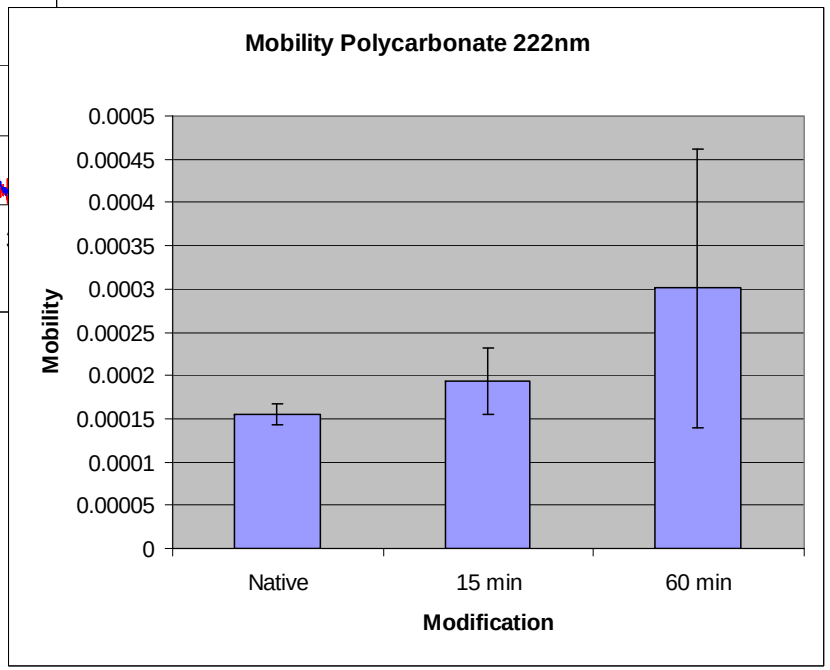
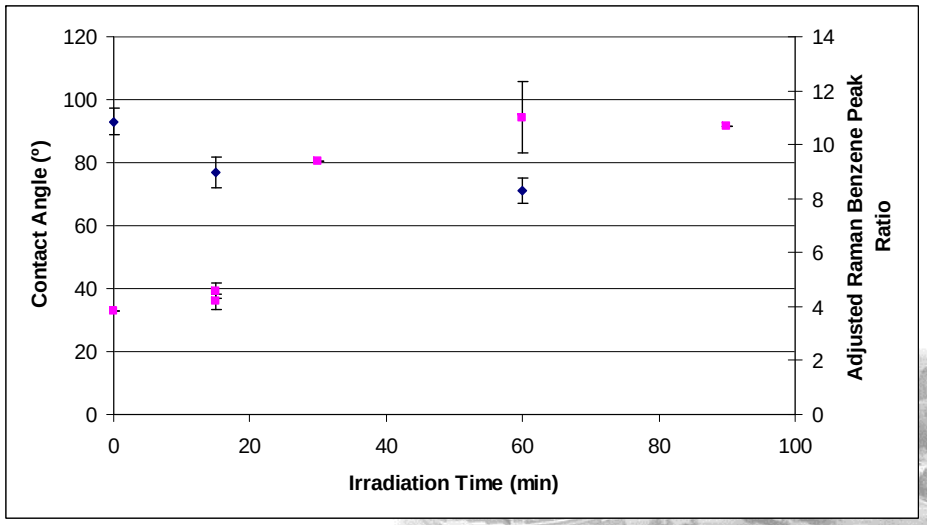
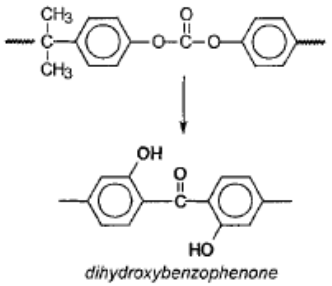
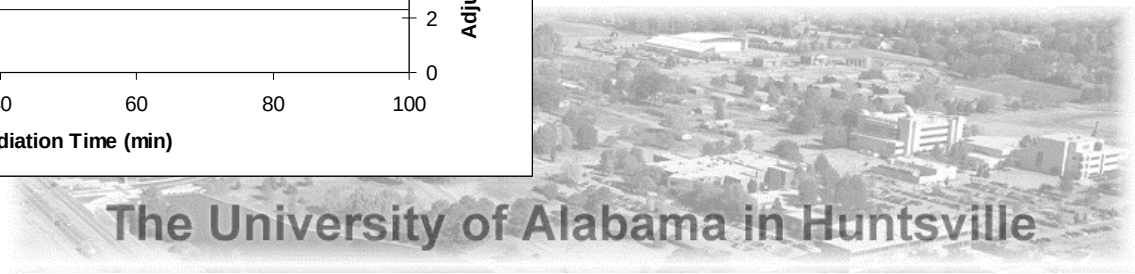
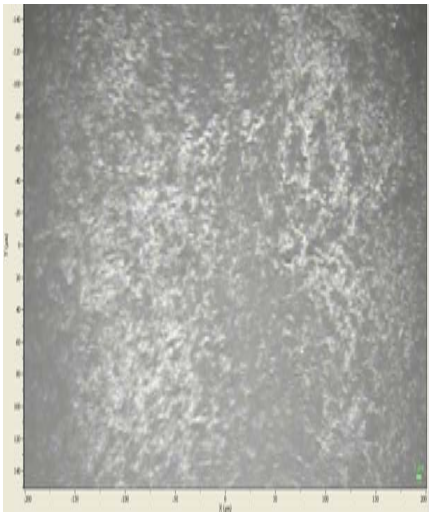

Raman Spectra of Polycarbonate Before (red) and After (blue)
60 Minutes of 222nm Radiation
Intensity (counts)
6000
5000
4000
3000
2000
1000
0
0
500
1000
1500
2000
2500
3000
Wavenumbers (cm-1)
para-substituted benzene ring deformation
benzeneC-C stretch

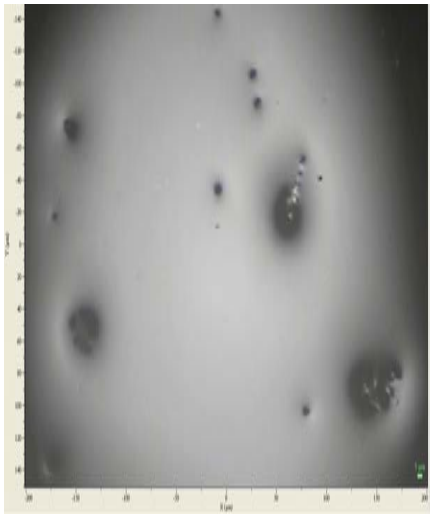

Mobility Polycarbonate 222nm
Mobility
0.0005
0.00045
0.0004
0.00035
0.0003
0.00025
0.0002
0.00015
0.0001
0.00005
0
Native
15 min
60 min
Modification

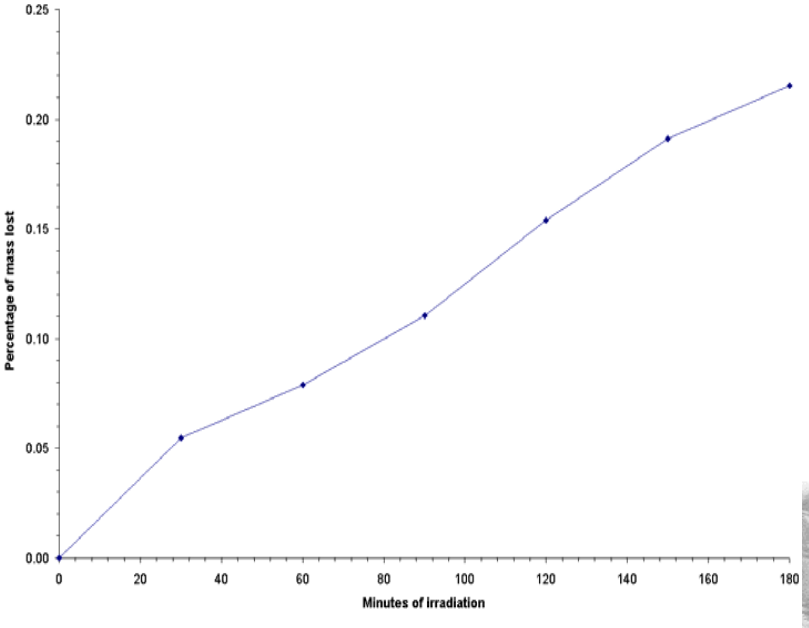

Contact Angle (°)
120
100
80
60
40
20
0
Adjusted Raman Benzene Peak Ratio
14
12
10
8
6
4
2
0
0
20
40
60
80
100
Irradiation Time (min)

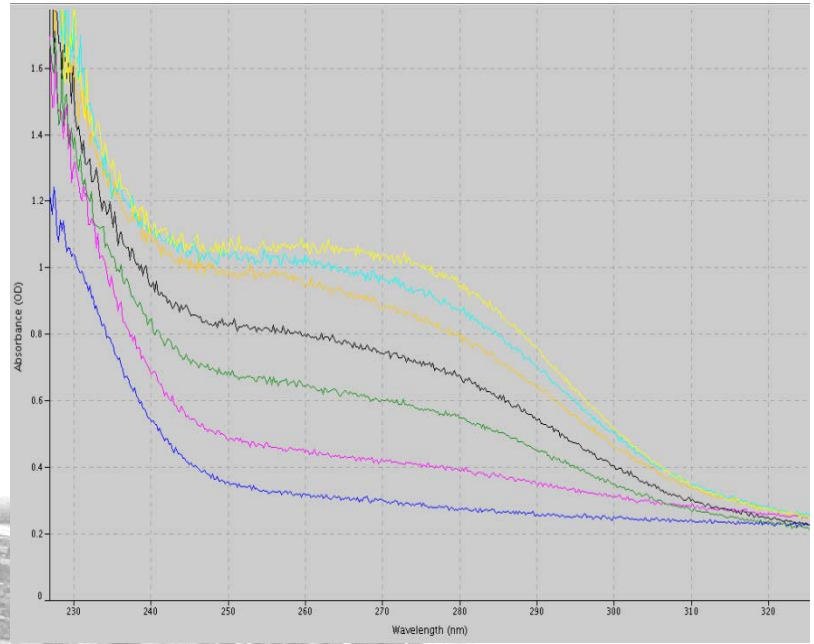

CH3
C
CH3
O
C
O
OH
O
C
HO
dihydroxybenzophenone


The University of Alabama in Huntsville









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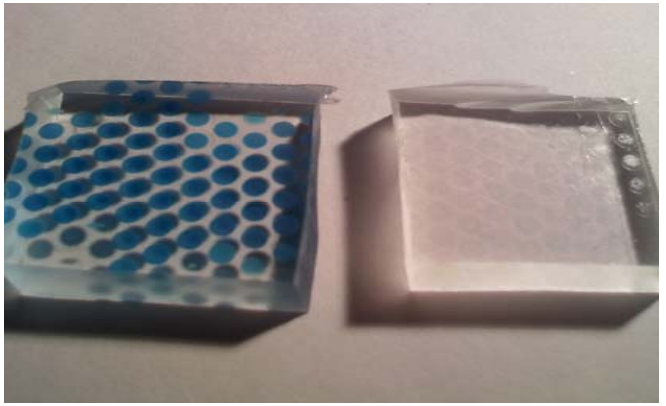
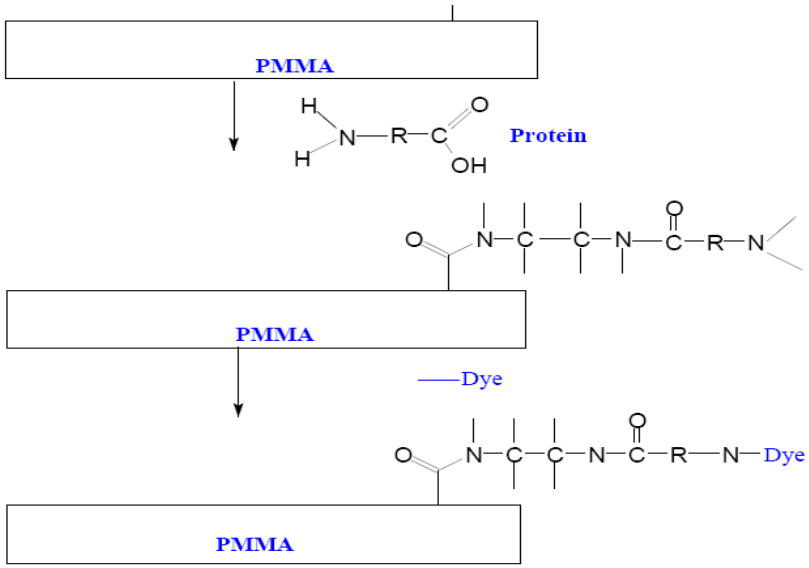
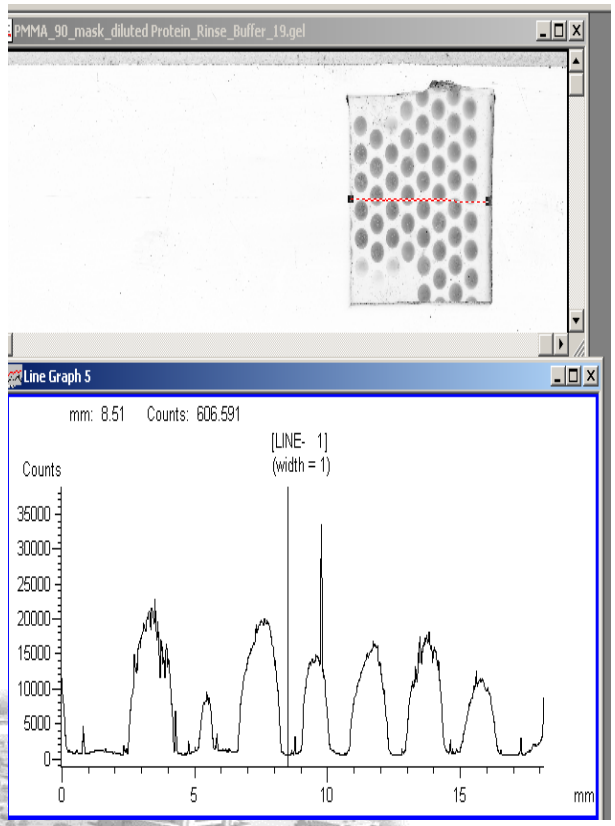
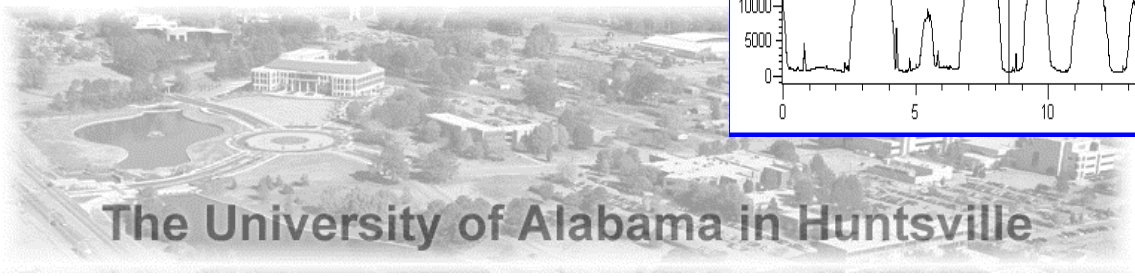
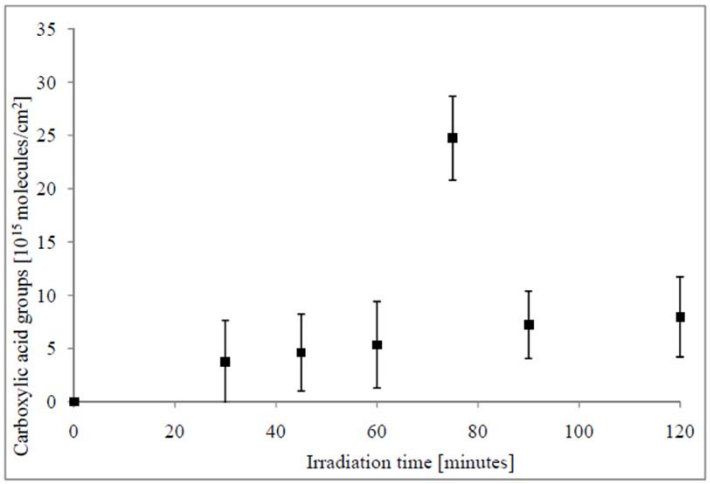
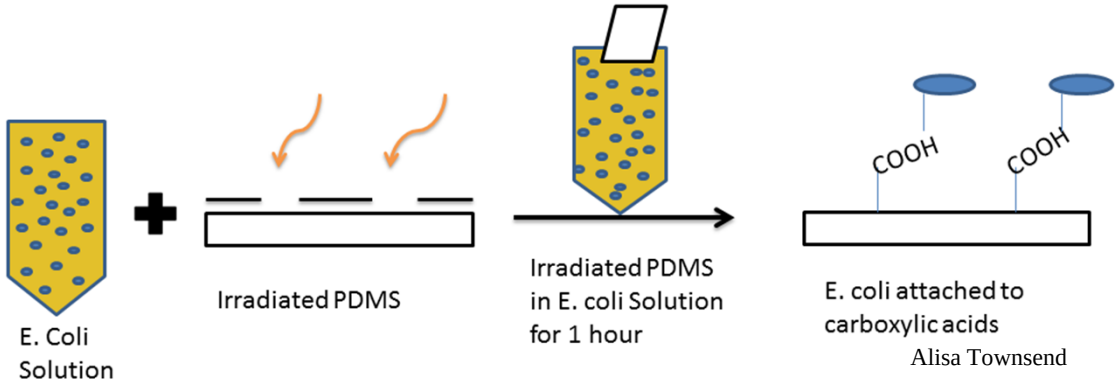



PMMA
Protein
PMMA
Dye
PMMA


PMMA_90_mask_diluted Protein_Rinse_Buffer_19.gel
Line Graph 5
mm: 8.51 Counts: 606.591
[LINE- 1]
(width = 1)
Counts
35000
30000
25000
20000
15000
10000
5000
0
0
5
10
15
mm

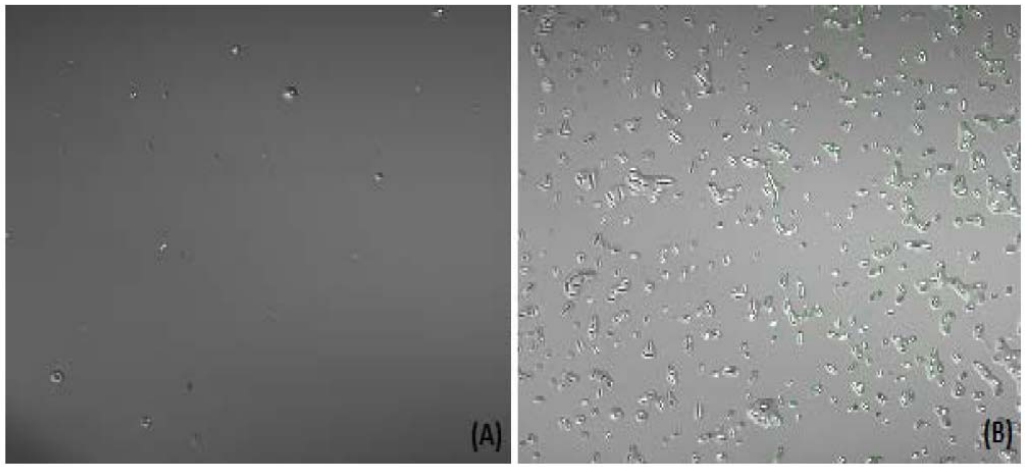

The University of Alabama in Huntsville



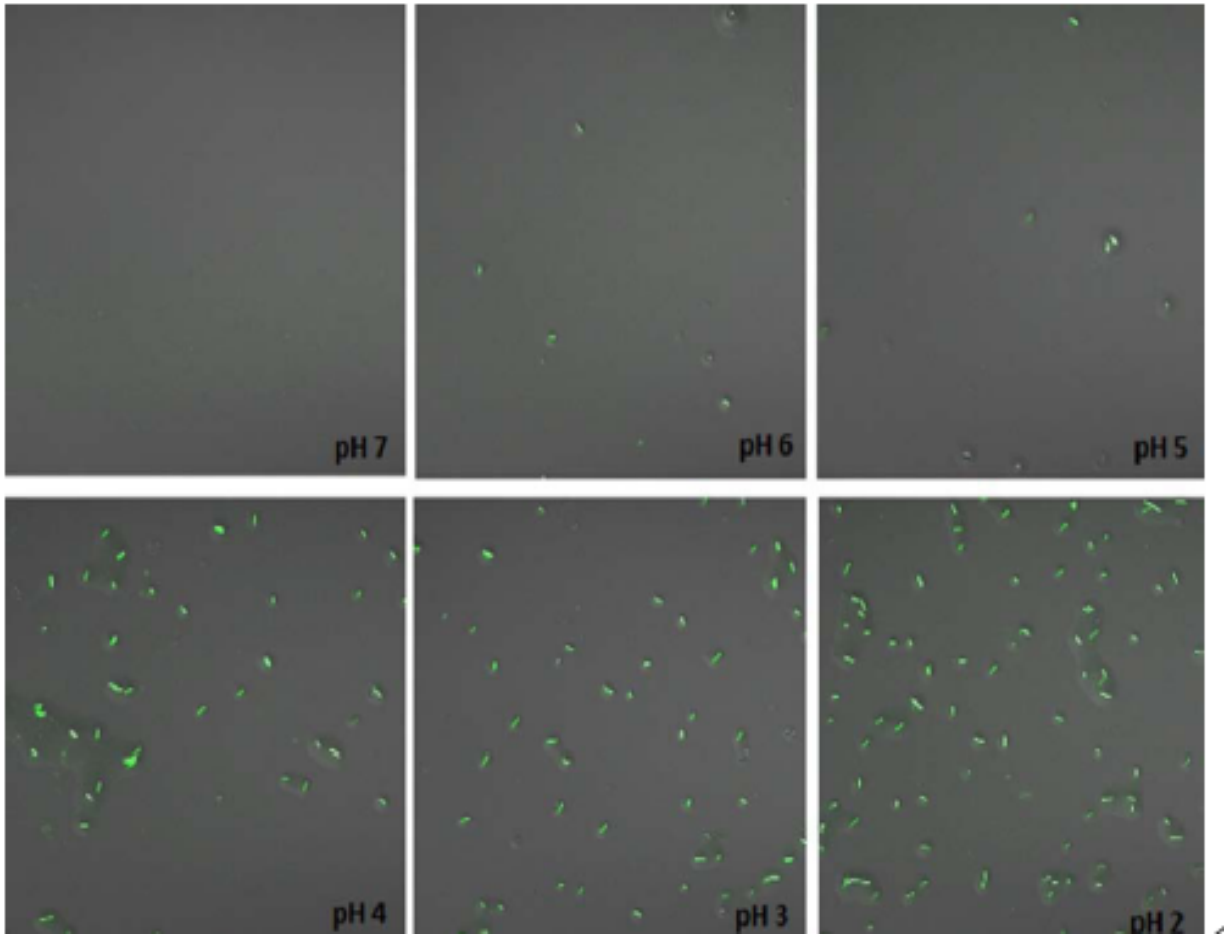


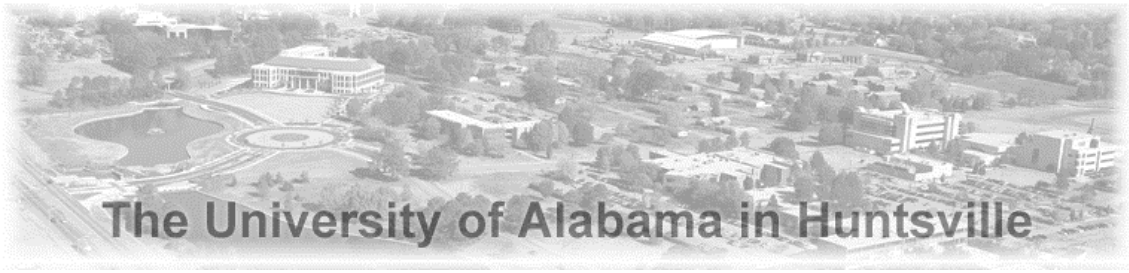
Alisa Townsend

Irradiated PDMS in M9 Media



E. coli, BL-21, grown in M9 media and exposed to irradiated PDMS. (A) represents irradiated PDMS placed in pH 7 M9 media culture. (B) represents irradiated PDMS placed in M9 media culture adjusted to pH 2. PDMS coupons placed in culture for one hour and rinsed with deionized water.


pH 7
pH 6
pH 5
pH 4
pH 3
pH 2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