Garcia Summer Scholars
Group 6

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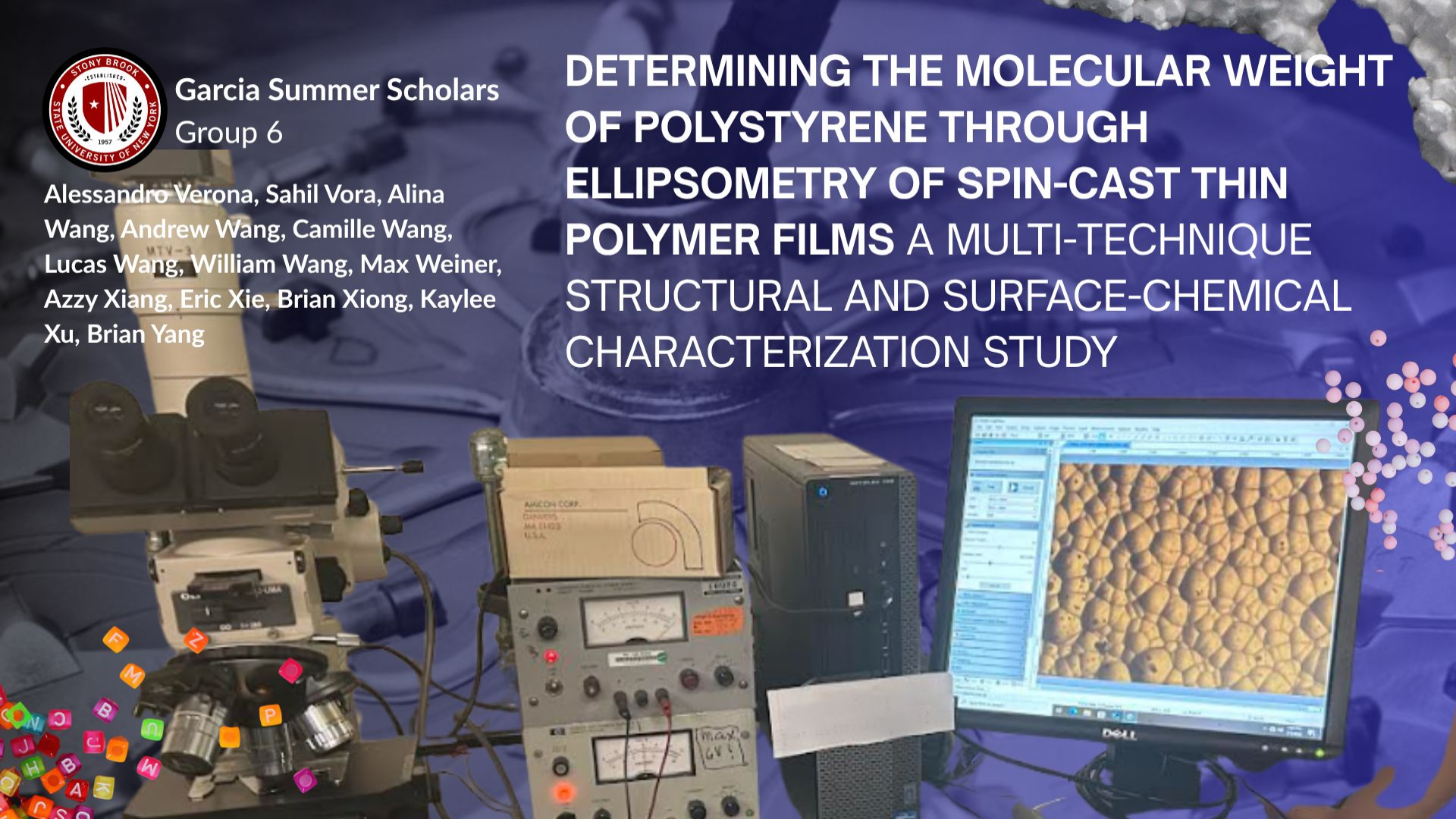
DETERMINING THE MOLECULAR WEIGHT OF POLYSTYRENE THROUGH ELLIPSOMETRY OF SPIN-CAST THIN POLYMER FILMS A MULTI-TECHNIQUE STRUCTURAL AND SURFACE-CHEMICAL CHARACTERIZATION STUDY



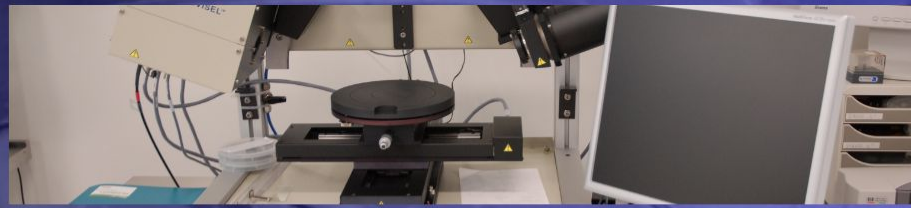
INTRODUCTION

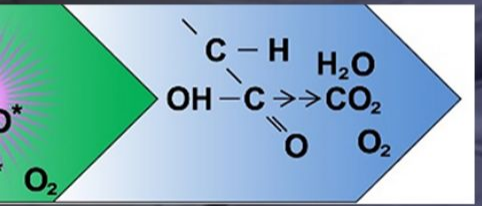
The waste problem

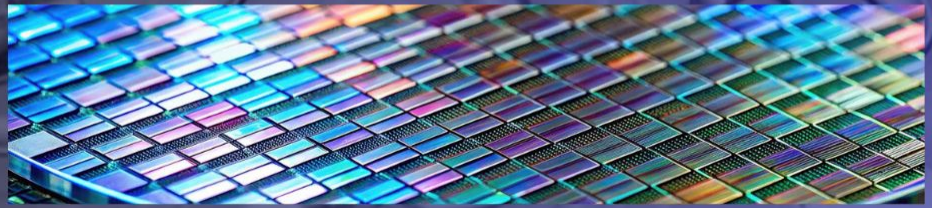
- 35.7 million tons of U.S. plastic waste in 2018; only 8.7% recycled; 8 million tons of plastic enter oceans yearly
- Saturated backbone resists microbial breakdown; it does not biodegrade without UV/ozone or high-energy exposure
- Molecular weight (*Mw*) controls melt viscosity and entanglement density — **it's the single number recyclers most need to know fast**
- Traditional Mw methods like viscometry need expensive equipment and long run times

The solution & study objectives

- Spin-cast ellipsometry is cheap, fast, single-measurement
- Process [100]-oriented Si wafers as clean, defect-free substrates; spin-cast a concentration series of a nominal 280,000 g/mol PS standard (Sigma-Aldrich) and measure film thickness by ellipsometry
- Back-calculate Mw from the concentration-thickness relationship; confirm chemical identity (FTIR) and thermal behavior (DSC); characterize UV/ozone surface oxidation via contact angle







[1] U.S. Environmental Protection Agency. Plastics: Material-Specific Data. Updated March 13, 2026. https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data.
[2] S. Sood, S. Fang, A. C. Wang, T. Luong, J. K. Kim, A. Sinha, J. Jerome, and M. H. Rafailovich, "Polystyrene laboratory analysis: A hands-on experience for high school students to determine the molecular weight of polystyrene through spin casting," Journal of Chemical Education, vol. 100, no. 2, pp. 900–906, 2023, doi: 10.1021/acs.jchemed.2c00987.

MATERIALS & METHODS

Material	Manufacturer	Specification
Atactic polystyrene	Sigma-Aldrich, St. Louis, MO	Nominal Mw = 280,000 g/mol
Toluene as solvent	Sigma-Aldrich, St. Louis, MO	ACS reagent grade
Silicon wafer	N/A, university stock	[100] Miller index, single-side polished
Kapton film	DuPont	Used to sandwich PS pellets during compression molding
Analytical balance	N/A, university stock	±0.1 mg resolution (4-digit)
Volumetric pipette	N/A, university stock	10.0 mL, ±0.05 mL uncertainty
Silicon cleaving tool	N/A, university stock	Diamond-tip scribe / diamond pen
Optical microscope	Metallurgical Olympus	10× and 50× objectives
DSC	TA Instruments Discovery DSC 250	20 °C/min ramp, 20-200 °C
Compression and hot press	Carver hot press	180 °C, 1000 lb, 4 min
FTIR spectrometer	Thermo Scientific Nicolet 6700	4000-400 cm^{-1} range
Spin coater	Headway Research PWM 32	2500 rpm, 30 s
Ellipsometer	Rudolph Research AutoEL	Null ellipsometry, 4 spots/sample
Contact angle goniometer	CAM 200 Optical Contact Angle Meter	Sessile drop, DI water
UV/Ozone chamber	N/A, university stock	Low-pressure Hg lamp

Table 1. Materials and manufacturer information.

$$Cp,\ app(T) = (dH/dt) / \beta.$$

DSC

$$A(\tilde{\nu}) = -\log_{10}[T(\tilde{\nu})] = \varepsilon(\tilde{\nu}) \cdot c \cdot l.$$

FTIR

$$\gamma SV = \gamma SL + \gamma LV \cdot \cos(\theta)$$

Contact Angle

$$\rho = rp/rs = \tan(\Psi) \cdot e^{i\Delta}.$$

Ellipsometry

DSC

5-20 mg sample placed in pan; temperature ramped from 20°C to 200°C

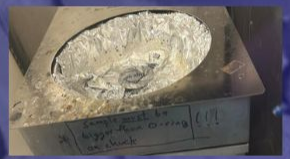
Compression Modeling

Sample of PS sandwiched in metal; temperature set to 180°C; 2,000 psi, 3,000-5,000 lbs of load; compress PS pellets into clear thin sheet; ran for 4 minutes

FTIR

FTIR directs IR through sample; records transmittance spectrum; serves as chemical footprint

Spin Coating



3-4 drops of PS solution on each silicon wafer; 2 wafers per concentration; spun at 2500 rpm for approx. 30 seconds

Ellipsometry

3 thickness measurements collected for each concentration of PS

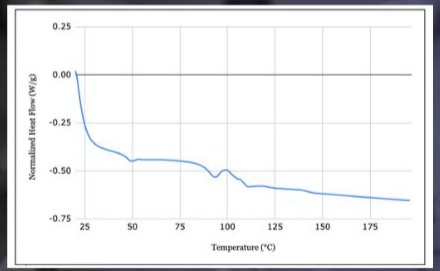
Contact Angle/UV Ozone

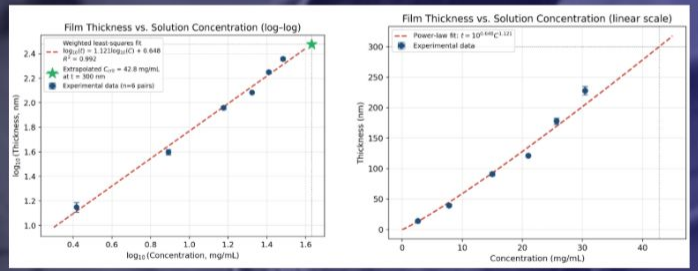
PS thin film wafers placed in UV/Ozone chamber; intervals of 0, 1, 2, 3 minutes; 3 contact angles collected for each data point

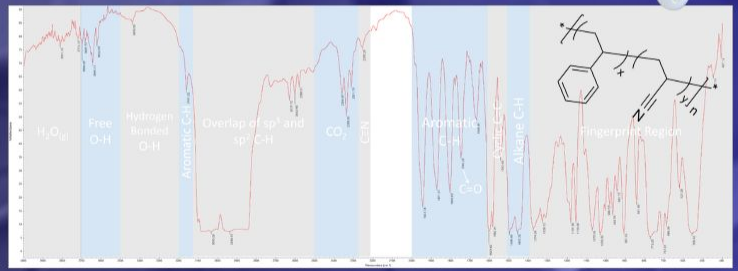
[3] Garcia Summer Scholars, "Spin casting polymer thin films" and "Determining the molecular weight of polystyrene through ellipsometry of spin casted thin polymer films," internal laboratory protocol and write-up instructions, 2026.

[4] A. C. Wang, S. Z. Chen, E. Xie, M. Chang, A. Zhu, A. Hansen, J. Jerome, and M. Rafailovich, "Utilizing machine learning to model interdependency of bulk molecular weight, solution concentration, and thickness of spin coated polystyrene thin films," MRS Communications, vol. 14, pp. 230–236, 2024, doi: 10.1557/s43579-024-00527-6.

RESULTS: IDENTITY







DSC

- Heat-flow trace shows a broad, continuous shift between 85-115 °C; the glass transition, centered around 100 °C
- No sharp melting peak anywhere in the 20–200 °C scan; confirms the sample is amorphous PS, not a semicrystalline impurity

ELLIPSOMETRY & THICKNESS

- Because spin-coating physics predicts a power law. thickness ∝ concentration to some exponent, we plotted log-log with linear
- **$\log_{10}(t) = 1.121 \cdot \log_{10}(C) + 0.648$, $R^2 = 0.992$** — an excellent fit across the whole concentration range

Wavenumber (cm^{-1})	Assignment
2938.6	sp^3 C–H stretch (backbone CH/CH_2)
1942.5 / 1871.6 / 1803.6	Overtone and combination bands of mono-substituted benzene ring out-of-plane bending
1745.8	Weak combination band; overlapping region; not attributable to a discrete PS fundamental
1605.5	Aromatic ring C=C stretch
1455.1	C–H bend and aromatic ring stretch
1378.9	CH_2/CH bending and ring in-plane mode
908.3	Aromatic C–H out-of-plane bend
841.8	Aromatic C–H out-of-plane bend
706.8	Mono-substituted benzene ring out-of-plane C–H bend
2336.9	Atmospheric CO_2; instrumental artifact, not sample-derived

FTIR & COMPRESSION

- Diagnostic peaks at 2938.6 cm^{-1} (aliphatic C–H stretch), 1605.5 & 1455.1 cm^{-1} (aromatic ring stretch), 706.8 cm^{-1} (mono-substituted benzene ring bend)
- The "comb" of three overtone bands at 1942.5 / 1871.6 / 1803.6 cm^{-1} are the classic signature of a phenyl ring

Pair	PS mass (mg)	Toluene vol. (mL)	Concentration (mg/mL)	Mean thickness (nm)	Thickness st.dev. (nm)
1	26.1 ± 0.1	10.00 ± 0.05	2.61 ± 0.02	14.1	1.3
2	77.8 ± 0.1	10.00 ± 0.05	7.78 ± 0.04	39.6	2.0
3	155.0 ± 0.1	10.00 ± 0.05	15.00 ± 0.08	91.0	3.1
4	210.0 ± 0.1	10.00 ± 0.05	21.00 ± 0.11	121.1	0.4
5	257.5 ± 0.1	10.00 ± 0.05	25.70 ± 0.13	178.4	4.8
6	304.3 ± 0.1	10.00 ± 0.05	30.43 ± 0.15	227.9	6.9

RESULTS: WEIGHT

- **Known MW: 280k g/mol**
- **Calculated: 265k ± 55k g/mol**
- **Error Percentage: 5.36%**

We define **Ccrit** as the concentration that would produce a 300 nm (3000 Å) film, a standard reference thickness. None of our 6 samples actually reached 300 nm, so we extrapolated the fitted line to find it.

A pre-established calibration curve links Ccrit to Mw. Compared to the manufacturer's nominal value of 2.80×10^5 g/mol, only 5.0% deviation — just 0.24σ off — well inside our propagated error bars. This validates the whole method.

- **Ccrit = 42.8 ± 2.8 mg/mL.**
- **$\log_{10}(\text{Ccrit}) = 3.378 - 0.322 \cdot \log_{10}(\text{Mw})$.**
- **$\text{Mw} = (2.66 \pm 0.55) \times 10^5$ g/mol.**

Molecular Weight in relation to thickness and concentration:

$$\log(Ccrit) = 3.378 - 0.322\log(MW)$$

where Ccrit is the concentration when the thickness is 300 nm.

From thickness (T) - concentration (C) equation:

$$\log(T) = 1.121\,\log(C) + 0.6483$$

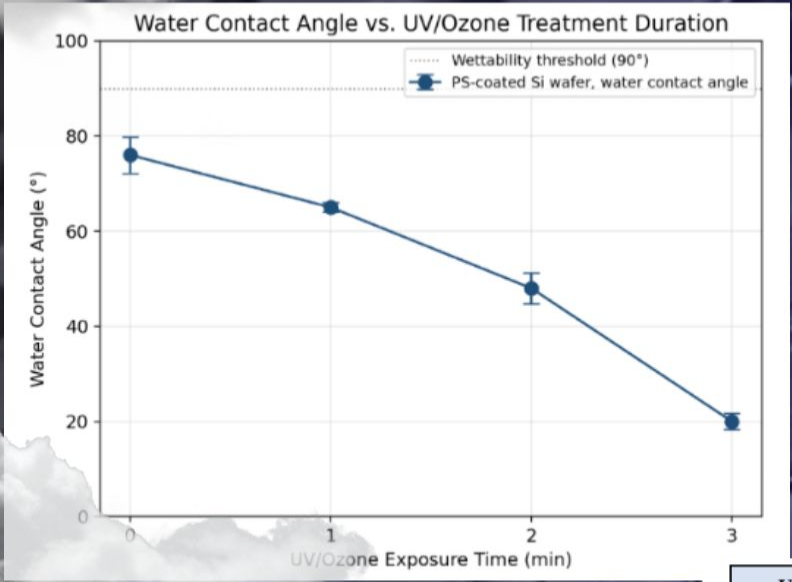
When T = 300 nm, Ccrit = 42.8

Thus, molecular weight (MW):

$$MW = 10^{(3.378-\log(Ccrit))/0.322} = 10^{(3.378-\log(42.8))/0.322} = 265,000\ g/mol$$

[5] B. Ren, E. Krasnoff, D. Bhat, D. Bhattacharya, I. Chan, A. Kiran, and M. Rafailovich, "Investigating the impact of bidispersity on spin-coated polystyrene thin films using machine learning," MRS Communications, published online Apr. 6, 2026, doi: 10.1557/s43579-026-00956-5.

RESULTS: UV/OZONE



- UV/ozone implants polar carbonyl and hydroxyl groups into the phenyl rings, raising surface energy and lowering contact angle via Young's equation
- The biggest single-interval drop (28°) happens between minutes 2 and 3; the effect accelerates, it doesn't plateau
- A quadratic fit captures this curve far better ($R^2 = 0.999$) than a straight line ($R^2 = 0.982$)
- This differs from some literature reports of an early plateau; possibly our UV/ozone source was more intense
- **Clear negative correlation, uncertainty relatively small, increased hydrophilicity**

- Bare, cleaned native-oxide Si wafer is typically 20–40°; strongly hydrophilic, due to polar Si-OH silanol groups
- After 3 minutes of UV/ozone, our PS surface (20°) matches or beats that range; UV/ozone can make a hydrocarbon polymer as wettable as glass
- **This is exactly why UV/ozone treatment is used to prep PS labware for cell culture — better wettability means better protein adsorption and cell adhesion**

UV/Ozone time (min)	θ1 (°)	θ2 (°)	θ3 (°)	Mean θ (°)	St. dev. (°)
0	80	74	73	76	3.8
1	64	66	65	65	1.0
2	49	50	44	48	3.2
3	22	19	19	20	1.7

[6] R. Kaizu, S. Takahashi, K. Hirose, K. Hatakeyama, G. V. Latag, A. Nomura, H. Tahara, and T. Hayashi, "UV/ozone treatment of polymer surfaces to enhance cell adhesion: The mechanism and guidelines for optimization," Langmuir, vol. 41, no. 43, pp. 29098–29110, 2025, doi: 10.1021/acs.langmuir.5c03398.
[7] R. J. Klein, D. A. Fischer, and J. L. Lenhart, "Systematic oxidation of polystyrene by ultraviolet-ozone, characterized by near-edge X-ray absorption fine structure and contact angle," Langmuir, vol. 24, no. 15, pp. 8187–8197, 2008, doi: 10.1021/la800134u.

ERROR PROPAGATION

$$\delta F(x,y)^2 = \left(\frac{dF}{dx}\delta x\right)^2 + \left(\frac{dF}{dy}\delta y\right)^2$$

$$\sigma f = \sqrt{[\ \Sigma i\ (\ \partial f/\partial xi\ )^2 \cdot \sigma xi^2\ ].}$$

$$s = \sqrt{[\Sigma(xi - \bar{x})^2 / (n-1)].}$$

$$\delta log,upper = log10(\bar{x} + s) - log10(\bar{x})$$

$$\delta log,lower = log10(\bar{x}) - log10(\bar{x} - s).$$

$$C = \frac{m}{V}$$

$$\delta C^2 = \left(\frac{1}{V}\delta m\right)^2 + \left(-\frac{m}{V^2}\delta V\right)^2.$$

Mean

$$\mu = \frac{\sum_{i=1}^{N} X_i}{N} \qquad \mu = \frac{a}{3} + \frac{b}{3} + \frac{c}{3}$$

$$\delta\mu^2 = \left(\tfrac{1}{3}\delta a\right)^2 + \left(\tfrac{1}{3}\delta b\right)^2 + \left(\tfrac{1}{3}\delta c\right)^2.$$

$$\sigma = \frac{\sqrt{a-\mu}}{3} + \frac{\sqrt{b-\mu}}{3} + \frac{\sqrt{c-\mu}}{3}$$

$$\delta\sigma^2 = \left(\delta a \tfrac{1}{6\sqrt{a-\mu}}\right)^2 + \left(\delta b \tfrac{1}{6\sqrt{b-\mu}}\right)^2 + \left(\delta c \tfrac{1}{6\sqrt{c-\mu}}\right)^2.$$

stdev

$$\sigma = \frac{\sum_{i=1}^{n}\sqrt{x_i-\mu}}{n}$$

Regression error

$$MW = f(C) = 10^{\frac{(3.378-\log(C))}{0.322}}. \qquad \delta f = \frac{f(C)}{0.322C}\delta C.$$

$$y = 1.121\,x + 06483. \qquad \delta x = \frac{\delta C}{C \cdot \ln(10)}$$

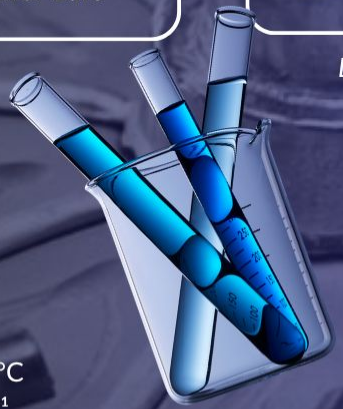
stdev

$$SE(\hat{x}_0) = \frac{\hat{\sigma}}{\hat{m}}\sqrt{\frac{1}{n} + \frac{(\hat{x}_0 - \bar{x})^2}{S_x}} \qquad \hat{\sigma} = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n-2}}, \text{ and } S_x = \sum_{i=1}^{n}(x_i - \bar{x})^2.$$

General Errors

- **Analytical balance:** ±0.1 mg
- **Volumetric pipette:** σV = 0.05 mL
- **Log-log regression:**
  - S = Σwi[log10(ti) − a·log10(Ci) − b]²
  - wi = 1/σlog(t),i²
  - ∂S/∂a = 0, ∂S/∂b
- **DSC temperature calibration:** ±0.1-0.3 °C
- **FTIR wavenumber calibration:** 0.48 cm^{-1}
- **Contact angle goniometer:** ±1.0° (t = 1 min) to ±3.8° (t = 0 min)

Error Bars



Concentration

Division

Thickness

Average/SD

Molecular Weight

Derivative; error in concentration; log-log

Pair	C (mg/mL)	σm/m (%)	σV/V (%)	σC/C (%)	σC (mg/mL)
1	2.61	0.383	0.500	0.630	0.016
2	7.78	0.129	0.500	0.516	0.040
3	15.00	0.065	0.500	0.504	0.076
4	21.00	0.048	0.500	0.502	0.105
5	25.70	0.039	0.500	0.501	0.129
6	30.43	0.033	0.500	0.501	0.152

Concentration (mg/mL)	Standard Deviation Error (nm)
2.61	0.305
7.78	0.248
15.00	0.197
25.70	0.469
30.43	0.145

[8] Rudolph Technologies, AutoEL III Automatic Ellipsometer Datasheet. [Online]. Available: Artisan Technology Group PDF copy.
[9] Greenwell, M. Brandon, and Christine M. Schubert Kabban. "investr: An R Package for Inverse Estimation." The R Journal, vol. 6, no. 1, 2014, pp. 90-100. doi: 10.32614/RJ-2014-009.

SOURCES OF ERROR

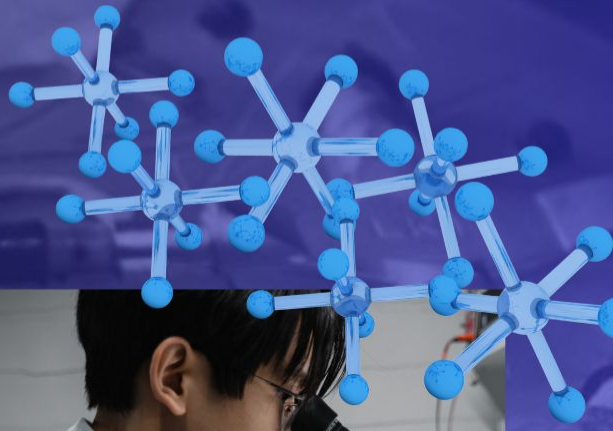
Potential errors

1. Human inconsistencies and manual placement
2. Beam-misalignment and equipment faults
3. Ambient temperature and humidity fluctuations
4. Minor lot-to-lot polydispersity in PS standard
5. CO_2 (2337 cm^{-1}) and H_2O (3200-3600 cm^{-1}) bands in FTIR

Error propagation conclusions

- Very small relative error in concentration and thickness, strong log-log linear relationship
- Larger uncertainty in final molecular weight calculation, though our data is accurate

Because our data is largely accurate and precise, we find that spin coating and ellipsometry is accurate and effective in determining the molecular weight of a polymer.



DISCUSSION & CONCLUSION

Implications

- Spin-cast ellipsometry gave an *Mw* estimate within 5% of the certified reference value, **a fast, low-cost method validated against a known standard**
- DSC and FTIR independently confirmed sample identity before we trusted the *Mw* number
- Full error propagation traced uncertainty from the balance and pipette all the way through the log-log regression to the final Mw, **dominant error source** was the calibration curve's amplification factor (3×)
- UV/ozone treatment demonstrated a controllable, fast way to tune PS surface wettability

Future work

- Extend UV/ozone exposure past 3 minutes to find the plateau
- Log spin-coating humidity and temperature to test the Meyerhofer thinning model directly
- Apply this exact workflow to an unknown or recycled PS sample as a real-world recycling quality control test

Cheaper alternative | **Fast and standardized**

Real-world use | **Backed by models**

THANK YOU!

Key supporting literature

LANGMUIR

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Article

UV/Ozone Treatment of Polymer Surfaces to Enhance Cell Adhesion: The Mechanism and Guidelines for Optimization

Riko Kaizu, Seiichiro Takahashi, Kenichi Hirose, Kenji Hatakeyama, Glenn Villena Latag, Ayano Nomura, Hiroyuki Tahara, and Tomohiro Hayashi*

Cite This: *Langmuir* 2025, 41, 29098−29110

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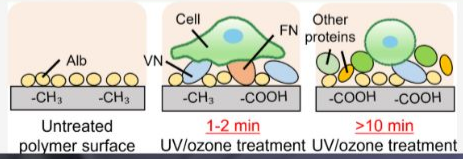

Langmuir **2008,** *24,* 8187−8197

Systematic Oxidation of Polystyrene by Ultraviolet-Ozone, Characterized by Near-Edge X-ray Absorption Fine Structure and Contact Angle

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Received January 15, 2008. Revised Manuscript Received April 23, 2008

The process of implanting oxygen in polystyrene (PS) via exposure to ultraviolet-ozone (UV-O) was systematically investigated using the characterization technique of near-edge X-ray absorption fine structure (NEXAFS). Samples of PS exposed to UV-O for 10−300 s and washed with isopropanol were analyzed using the carbon and oxygen *K*-edge NEXAFS partial electron yields, using various retarding bias voltages to depth-profile the oxygen penetration into the surface. Evaluation of reference polymers provided a scale to quantify the oxygen concentration implanted by UV-O treatment. We find that ozone initially reacts with the double bonds on the phenyl rings, forming carbonyl groups, but within 1 min of exposure, the ratio of double to single oxygen bonds stabilizes at a lower value. Oxygen penetrates the film with relative ease, creating a fairly uniform distribution of oxygen within at least the first 4 nm (the effective depth probed by NEXAFS here). Before oxygen accumulates in large concentrations, however, it preferentially degrades the uppermost layer of the film by removing oxygenated low-molecular-weight oligomers. The failure to accumulate high concentrations of oxygen is seen in the nearly constant carbon edge jump, the low concentration of oxygen even at 5 min exposure (58% of that in poly(4-acetoxystyrene), the polymer with the most similarities to UV-O-treated PS), and the relatively high contact angles. At 5 min exposure the oxygen concentration contains ca. 7 atomic % oxygen. The oxygen species that are implanted consist predominantly of single O−C bonds and double O═C bonds but also include a small fraction of O−H. UV-O treatment leads a plateau after 2 min exposure in the water contact angle hysteresis, at a value of 67 ± 2°, due primarily to chemical heterogeneity. Annealing above T_g allows oxygenated species to move short distances away from the surface but not diffuse further than 1−2 nm.

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Laboratory Experiment

Polystyrene Laboratory Analysis: A Hands-On Experience for High School Students to Determine the Molecular Weight of Polystyrene Through Spin Casting

Sahil Sood,* Sean Fang, Alexander Chengyu Wang, Thomas Luong, Justin Keonhyoung Kim, Arkajyoti Sinha, John Jerome, and Miriam H Rafailovich

Cite This: *J. Chem. Educ.* 2023, 100, 900−906

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ABSTRACT: Hands-on learning is a staple in high school science education, as it provides students with a fast-learning curve and a great degree of field competency. However, due to the safety risks associated with high school students in university chemistry laboratory settings, high school students rarely engage in authentic hands-on chemical learning. To bridge the gap between the benefits and drawbacks, this study investigates a method to educate high school students (with no previous experience) about standard chemical laboratory practices. 98 high school students experimented throughout 2 days to determine the molecular weights and characteristics of various polystyrene samples, essential knowledge for polymer recycling. Students were split into 5 groups so that laboratory usage be organized and staggered. After laboratory