Synthesis and Patterning of Thin Films using Spin-Coating Ring Opening Metathesis Polymerization on Self-Assembled Monolayers

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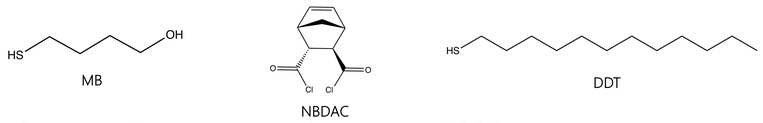
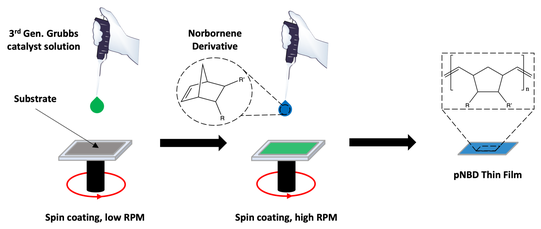
Introduction

- Spin-coating ring opening metathesis polymerizaiton (scROMP) combines the efficiency of ROMP, a well-studied technique used to polymerize cyclic olefin monomers, and the rapid synthetic process of spin-coating.
- Polymerizing via scROMP on different self assembled monolayers (SAMs) yield varying film characteristics, such as **uniformity** and **thickness**. In this study, **1-mercapto-4-butanol (MB)**, ***trans*-5-norbornene-2,3-dicarbonyl chloride (NBDAC)**, and **1-dodecanethiol (DDT)** were used to form different combinations of SAMs on gold substrates.



- Due to the inert methyl-terminated ends of DDT molecules, the catalyst "slides" off the substrate during scROMP, resulting in irregular films.
- Through harnessing the different properties of SAMs, **can polymer films be patterned onto substrates using scROMP?**

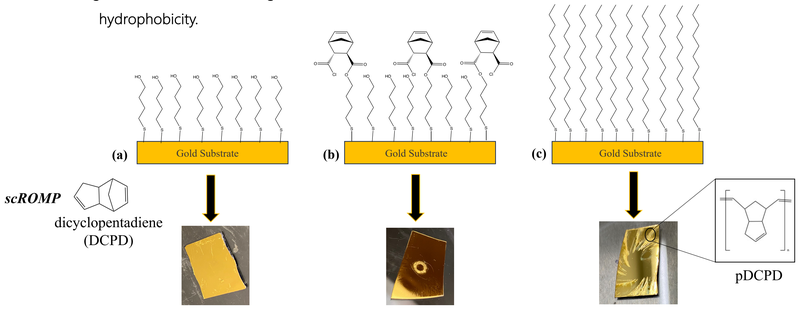


Schematic of the experimental approach for scROMP

SAMs Influence Surface Properties

- Sessile water contact angles were used to characterize the surface of the SAMs.
- Contact angles increase with increasing hydrophobicity.

	MB (a)	MB + NBDAC (b)	DDT (c)
Sessile Contact Angle (°)	38 ± 3	59 ± 4	99 ± 6



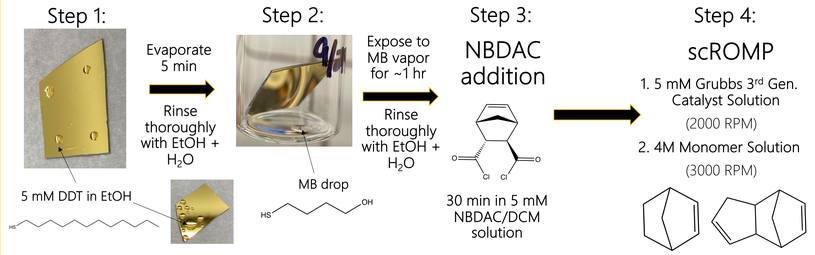
- The catalyst interacts efficiently with the hydroxyl (a) and alkene (b) terminated monolayers, promoting more **uniform** films.
- Further profilometry data must be obtained to establish a concrete trend between **monolayer type + film thickness**.

	Roughness (nm)	Average Step Height (µm)
No Monolayer	175	7.03
MB (a)	150	6.77
MB + NBDAC (b)	180	5.70
DDT (c)	84*	6.53

*DDT roughness was recorded on a portion of the substrate that did not appear to have a film.

scROMP on Dual Monolayers

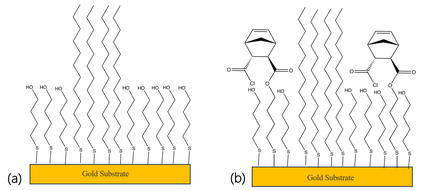
Synthesis of Dual Monolayer:

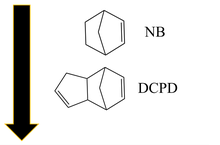


Characterization of Dual Monolayer:

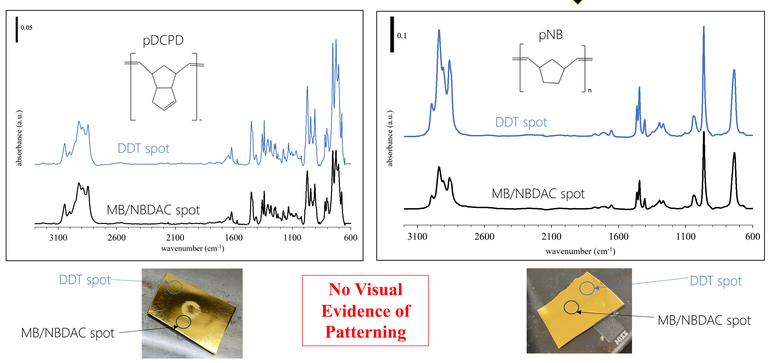
- Sessile water contact angles were used to characterize the surface of the dual SAMs.
- Small DDT "spots" were **hard to find** at times, but once located, differences in contact angles between MB/NBDAC and DDT areas were apparent and consistent with previous data.
- When close to a border, water drops would "jump" from the hydrophobic region to the near-by hydrophilic region.

	MB	DDT	MB + NBDAC	DDT
Sessile Contact Angle (°)	36 ± 4	95 ± 3	56 ± 4	94 ± 3
			Before NBDAC addition (a)	After NBDAC addition (b)



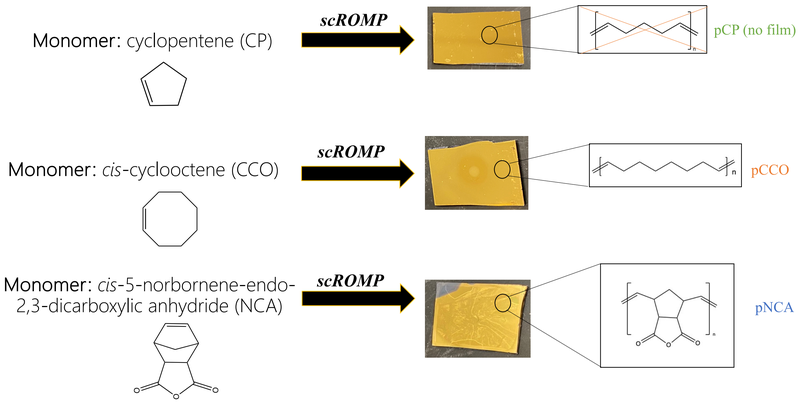


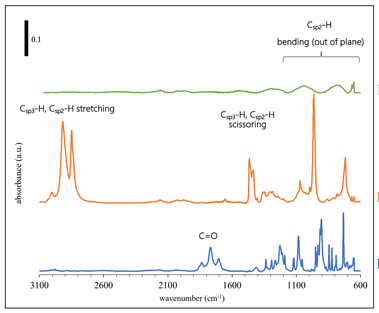
Characterization of "Patterned" Film:



- Lack of patterning is supported by FTIR spectra.
  - Polymerization is still occurring on the "slick" DDT areas.
  - In past studies of area-selective vapor phase deposition patterning, low selectivity is often observed due **to inevitable nucleation of polymers on non-growth areas.**[1]
- Further experimentation is necessary to better understand how polymerization occurs on a DDT monolayer.
  - What are the cause of the "striations"? Can the irregular films formed on DDT SAMs be predicted and controlled?

Synthesizing New scROMP Polymers





- Polymerizing CP via scROMP was unsuccessful, likely due to the **low ring strain** and **high vapor pressure** of the monomer.[2]
- FTIR suggests polymerization of CCO and NCA occurred.
- Broadens the library of monomers available for scROMP.

Conclusions

- Performing scROMP on different SAMs yields films with different surface properties due to catalyst-monolayer interactions.
- Results of surface patterning using dual SAMs are inconclusive. Further investigation is necessary to better understand the surface chemistry of a DDT monolayer.
- pCCO and pNCA were synthesized for the first time using the scROMP method. CP is not a favorable monomer for scROMP due to its low ring strain and high vapor pressure.

References:

1. Qiu, M., et. al. Recent Progress in Non-Photolithographic Patterning of Polymer Thin Films. Prog. Polym. Sci. **2023**, 142, 101688.
2. Mulhearn, W. D.; Register, R. A. Synthesis of Narrow-Distribution, High-Molecular-Weight ROMP Polycyclopentene via Suppression of Acyclic Metathesis Side Reactions. ACS Macro Lett. **2017**, 6 (2), 112–116.

Acknowledgements

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