

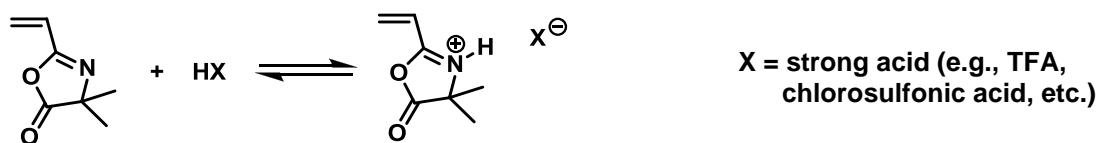
Superhydrophobic Thin Films Fabricated by Reactive Layer-by-Layer Assembly of Azlactone-Functionalized Polymers

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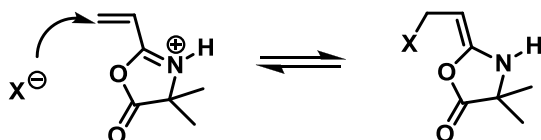
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Supporting Information

Monomer activation:



Initiation:



Propagation:

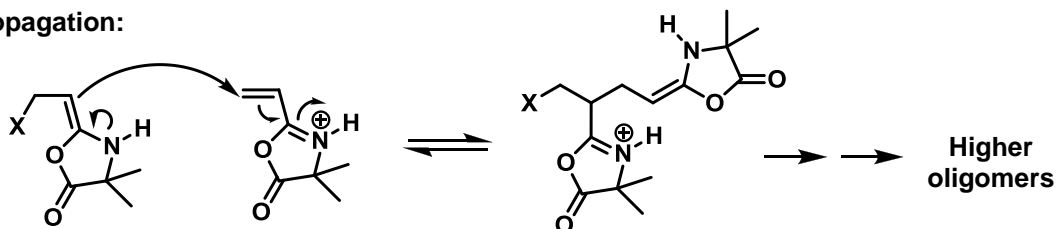


Figure S1. Activation, initiation, and propagation of the acid-catalyzed oligomerization of VDMA as proposed by Heilmann et al.¹ The nitrogen of the azlactone ring is protonated by a strong acid to activate the azlactone ring. A counterion then adds to the activated monomer by Michael Addition to the olefin, forming an enol-like intermediate. This enol-like tautomer can then undergo a subsequent Michael Addition reaction with an additional unit of activated monomer to form the dimer. This process can propagate to form higher order oligomers (i.e., trimers, tetramers, pentamers, etc.; see Figure S2 for structures).

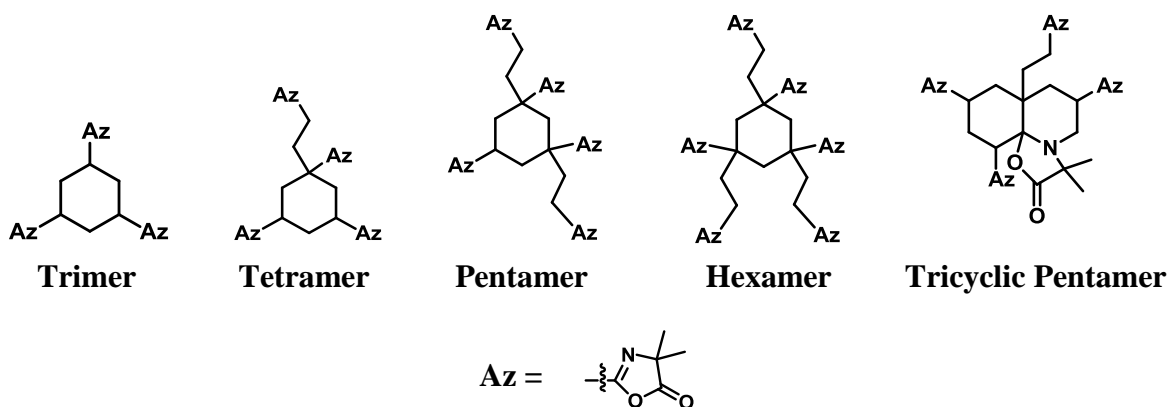


Figure S2. Structures of cyclic oligomers formed during oligomerization, as proposed by Heilmann et al.¹

Table S1. LC-MS characterization of oligomer precipitated from non-distilled monomer. The oligomers were hydrolyzed prior to LC-MS analysis to improve solubility in aqueous solvents and the resolution of the peaks on the LC column, as described previously by Heilmann et al.¹

M_w	MS assignment ^a
158	Monomer + 1H ₂ O
315	Dimer + 2H ₂ O
472	Trimer + 3H ₂ O
611	Tetramer + 3H ₂ O
629	Tetramer + 4H ₂ O
768	Pentamer + 4H ₂ O
784	Pentamer + 5H ₂ O
925	Hexamer + 5H ₂ O
941	Hexamer + 6H ₂ O

^a Mass spectrometry notations refer to the extent of hydrolysis of each oligomeric structure. For example, “Tetramer + 3H₂O” indicates that 3 out of 4 azlactone rings have been hydrolyzed.

Table S2. LC-MS characterization of intentionally synthesized oligomers. The oligomers were hydrolyzed prior to LC-MS analysis to improve solubility in aqueous solvents and the resolution of the peaks on the LC column, as described previously by Heilmann et al.¹

M_w	MS assignment ^a
418	Trimer
472	Trimer + 3H ₂ O
629	Tetramer + 4H ₂ O
732	Pentamer + 2H ₂ O
768	Pentamer + 4H ₂ O
871	Hexamer + 2H ₂ O

^a Mass spectrometry notations refer to the extent of hydrolysis of each oligomeric structure. For example, “Tetramer + 3H₂O” indicates that 3 out of 4 azlactone units have been hydrolyzed.

References

1. Heilmann, S. M.; Moren, D. M.; Krepski, L. R.; Rasmussen, J. K.; Gaddam, B. N.; Roscoe, S. B.; Lewandowski, K. M.; McIntosh, L. H.; Roberts, R. R.; Fansler, D. D.; Szekely, G. G.; Weil, D. A.; Thakur, K. A.; Pathre, S. V.; Battiste, J. L.; Hanggi, D. A., *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2003**, A40, 755-790.