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SCIENCE

Polymer-based Transient Electronics *via* Oligo-3-hexylthiophene Grafted to Degradable Polymer Backbone

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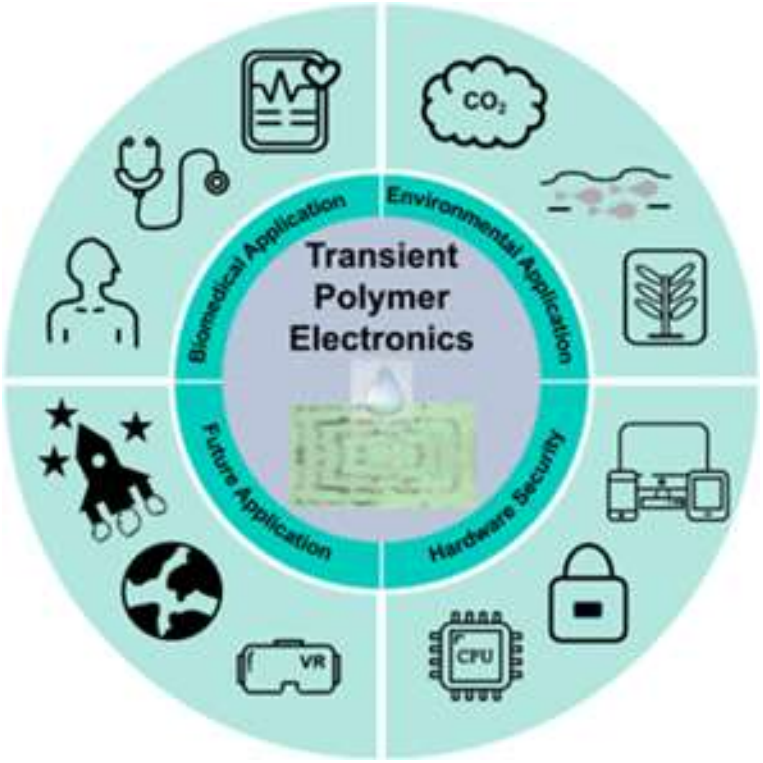
What is Transient Electronics?

- Electronic materials that are intentionally degraded to environmentally benign materials.
- Applications in skin electronics and implantable medical electronics, such as in health monitoring, diagnostics, and therapeutics.
- Conformability, stretchability, biocompatibility and biodegradability.
- Conducting polymers can be chemically modified for functionality.
- Transience challenging due to chemically rigid, macromolecular nature.



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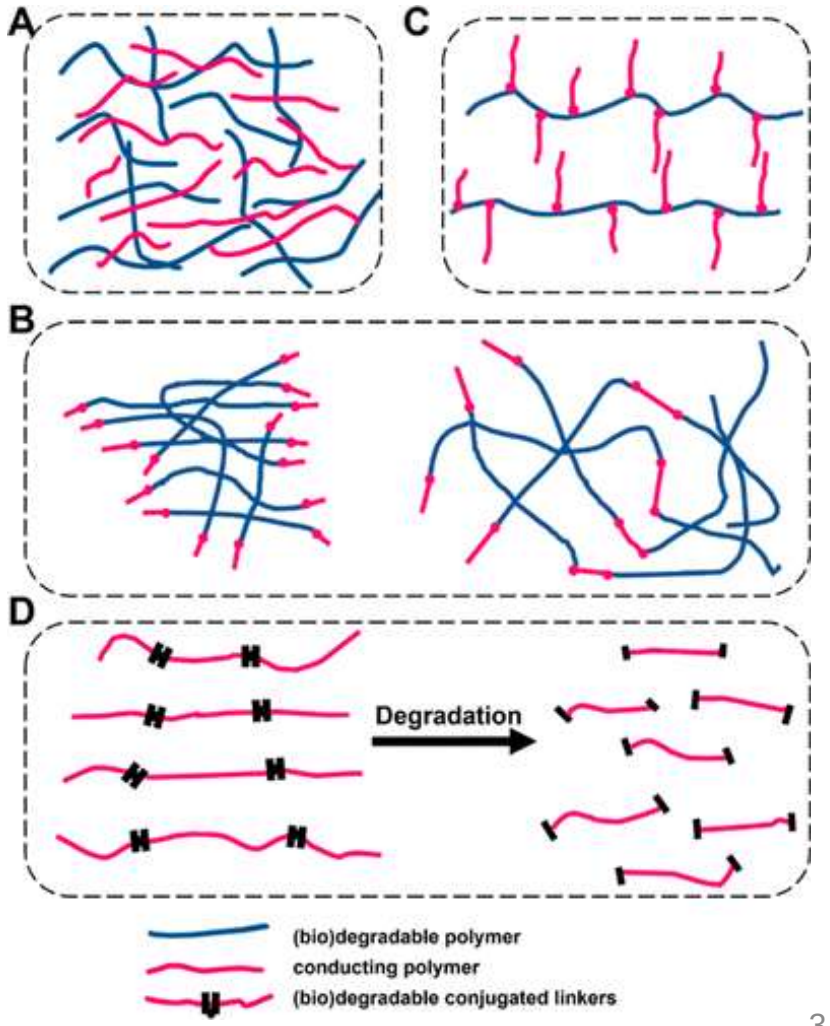
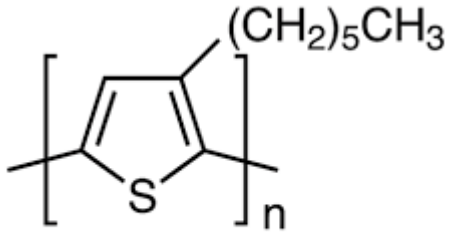
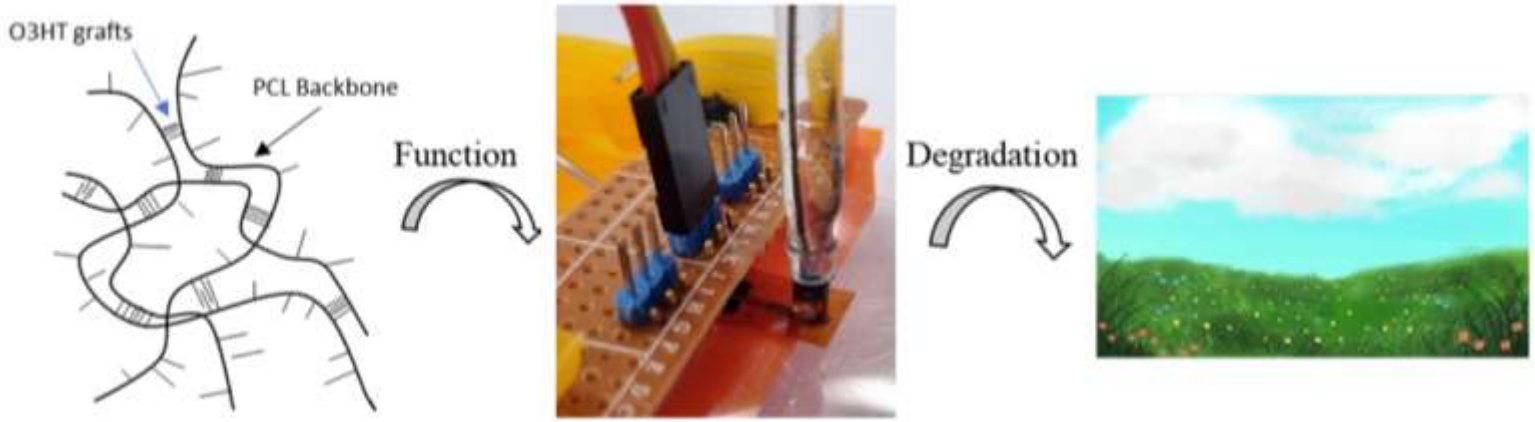
Existing CP-based Transient Electronics

- Composites of CPs and degradable polymers.
- Conductive oligomers attached to the ends of (bio)degradable polymer backbone or as crosslinker.
- Grafting to biodegradable polymers.
- Conductive polymers with (bio)degradable conjugated linkers.



Project Aim





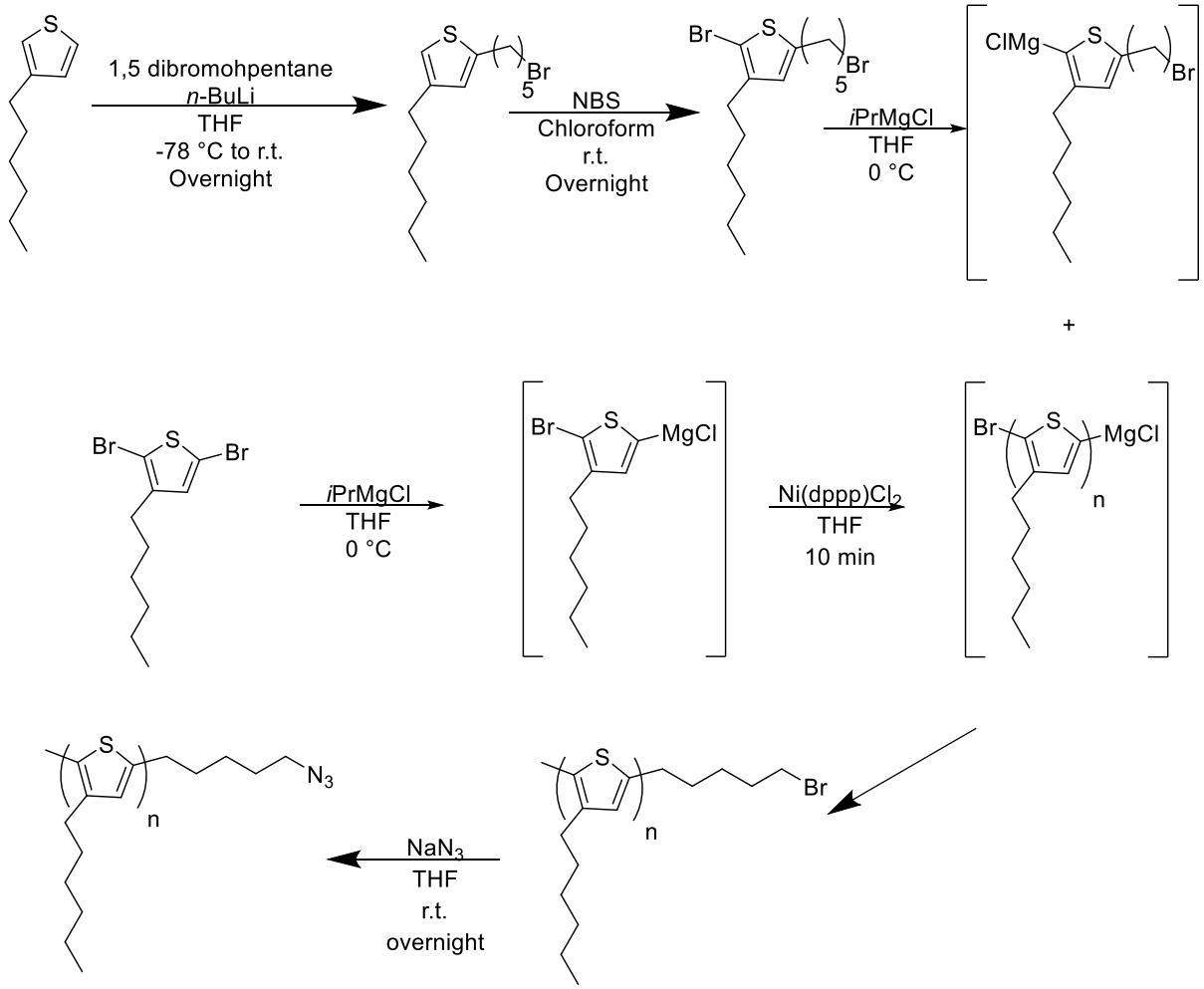
- Make transient electronics, *via* attachment of oligomers to a biodegradable backbone. Conductivity is expected to be enhanced due to crystalline domain *via* π-π stacking interaction.

- Short segments of oligomers chosen due to their better solubility than polymers, 3-hexylthiophene (3HT) chosen for its ease of solubility and stability.

- Degradable polymer polycaprolactone (PCL) used as backbone.

Synthesis of O3HT

Oligomer Synthesis

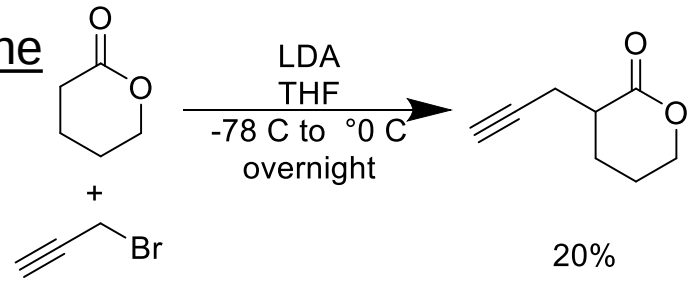


- Oligomerisation of 3-Hexylthiophene using Kumada coupling.
- Molecular weight can be controlled *via* amount of catalyst used, with DI of ~1.3.

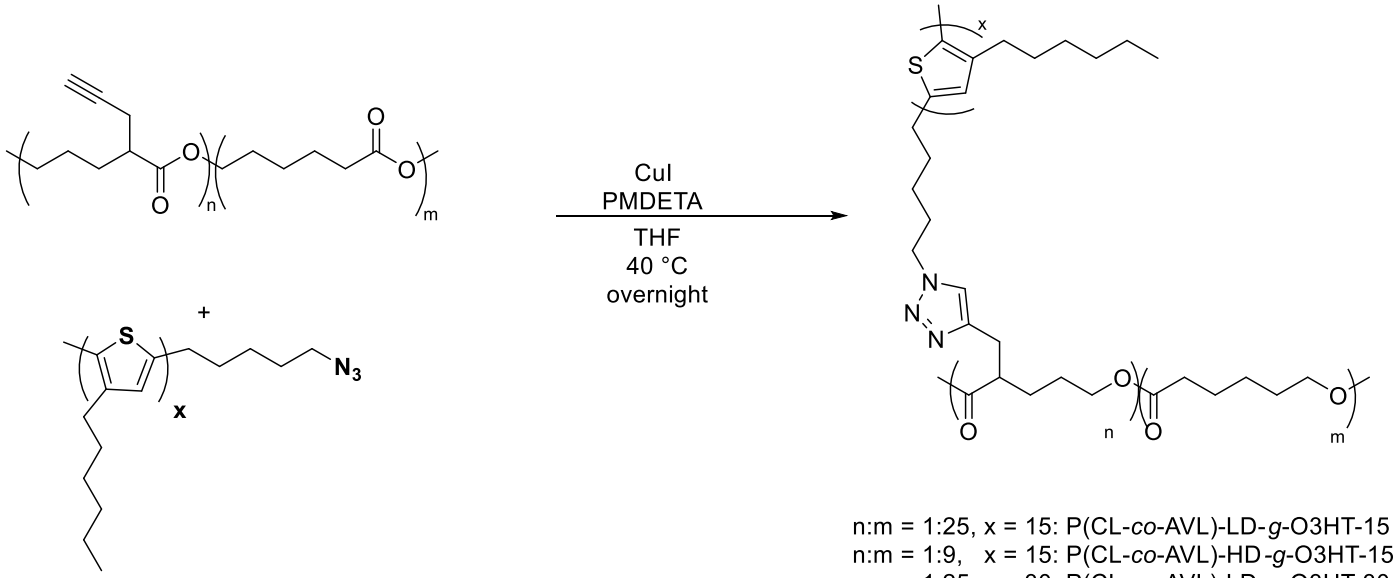
Sample	Mn (Da)	Mw (Da)	PDI	Length (units)
O3HT-15	2449	3083	1.26	15
O3HT-30	3802	5114	1.35	30
O3HT-40	6183	7983	1.29	42

Synthesis of Degradable Backbone

δ-valerolactone with alkyne

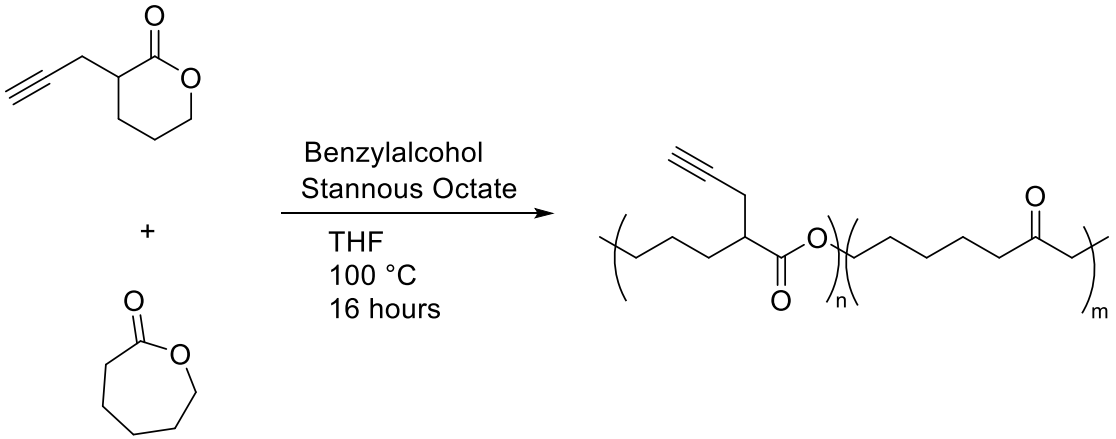


Attachment to form P(CL-*co*-AVL)-*g*-O3HT



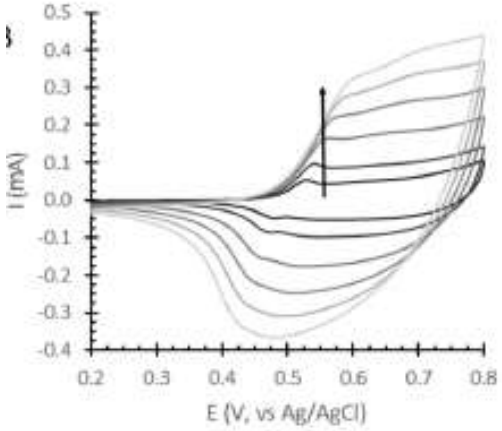
n:m = 1:25, x = 15: P(CL-*co*-AVL)-LD-*g*-O3HT-15
n:m = 1:9, x = 15: P(CL-*co*-AVL)-HD-*g*-O3HT-15
n:m = 1:25, x = 30: P(CL-*co*-AVL)-LD-*g*-O3HT-30
n:m = 1:9, x = 30: P(CL-*co*-AVL)-HD-*g*-O3HT-30

Polymerisation to form P(CL-*co*-AVL)

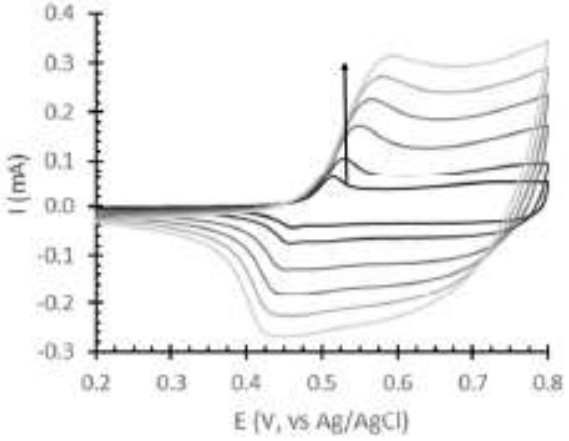


- Different **lengths** of oligomers were attached at different density to the modified PCL.
- **Density** modulated by ratio of δ-valerolactone to caprolactone used.

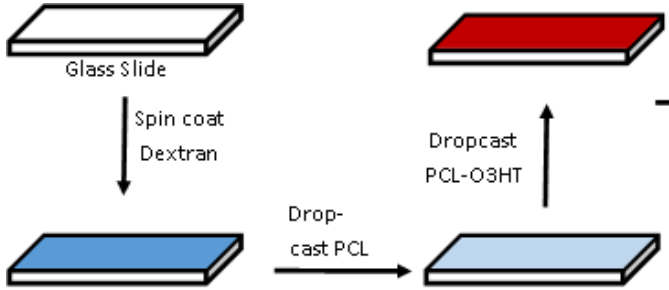
Electrochemical Properties

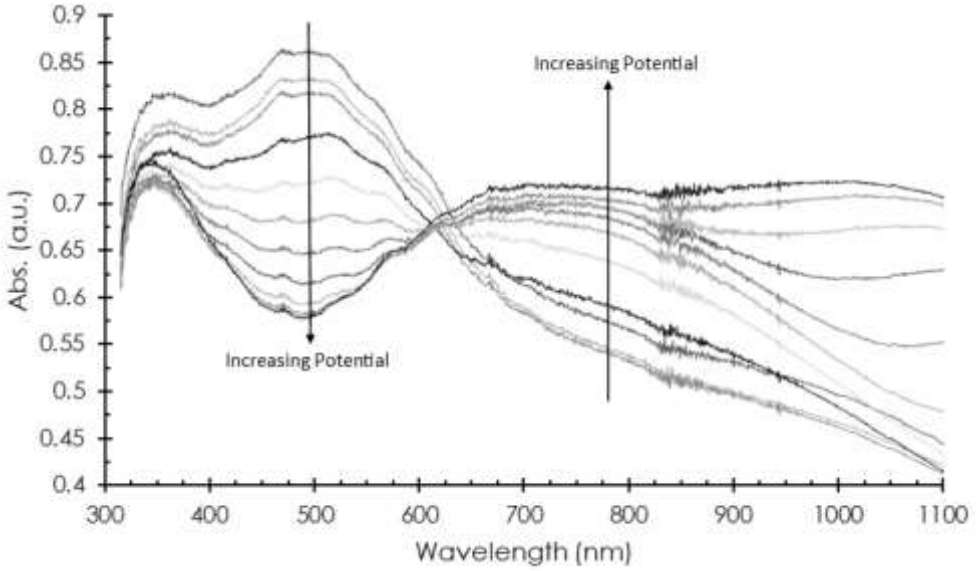


O3HT-**30**



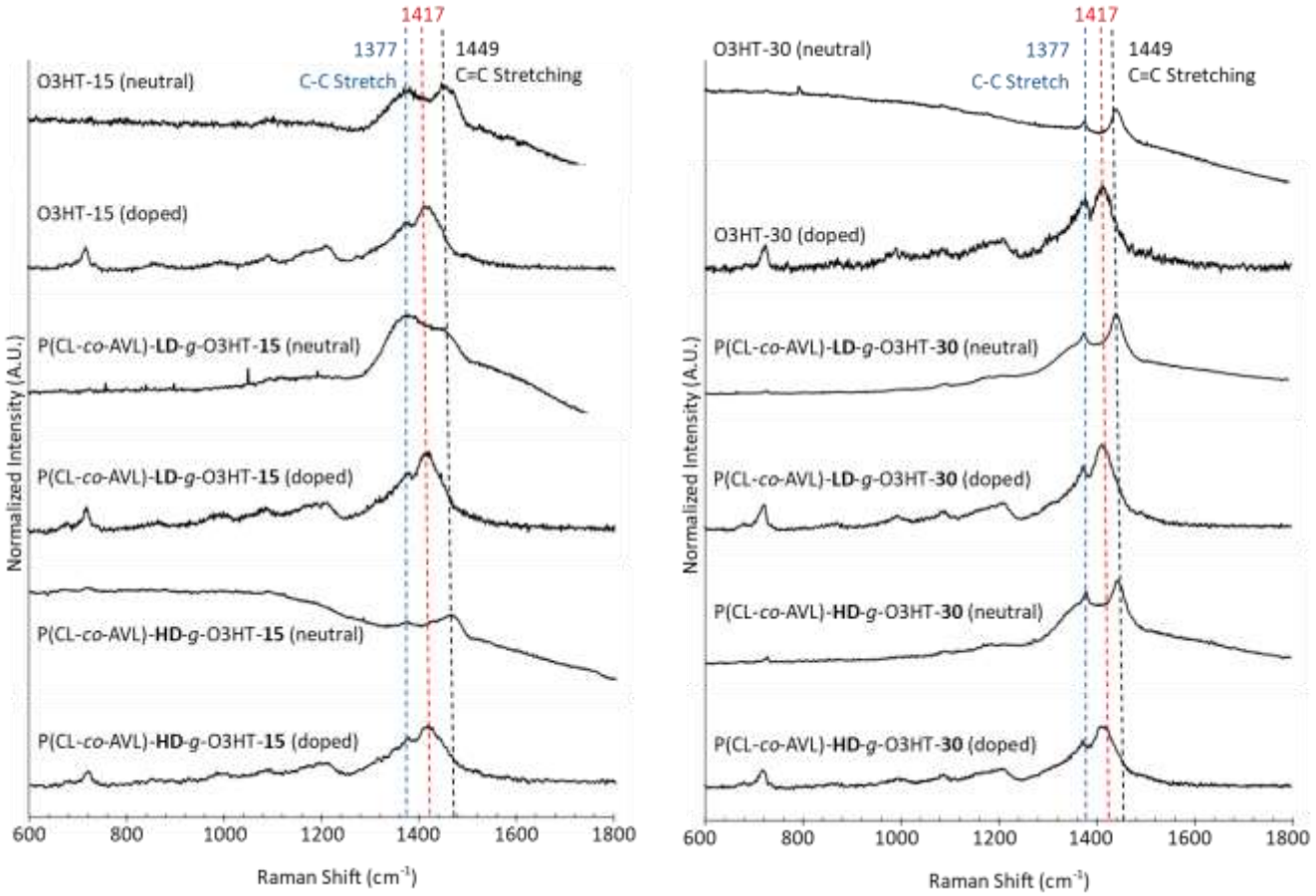
P(CL-*co*-AVL)-**LD**-*g*-O3HT-**30**





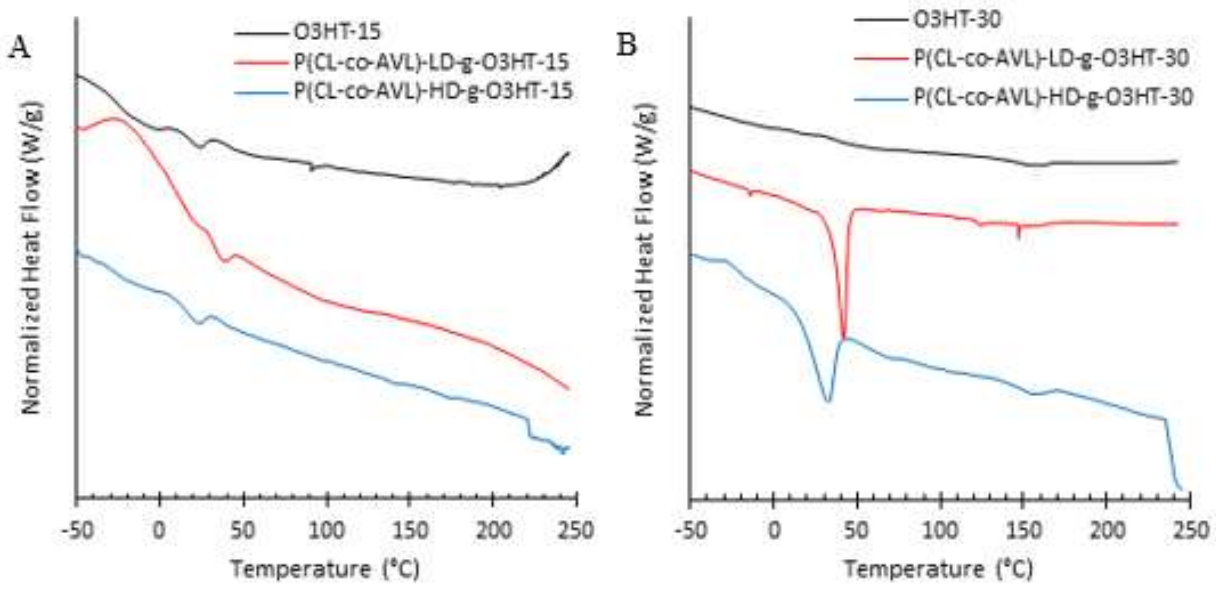
Sample	Conductivity (S cm^{-1})
P(CL-*co*-AVL)-**LD**-*g*-O3HT-15	0.003 ± 0.0002
P(CL-*co*-AVL)-**HD**-*g*-O3HT-**15**	0.234 ± 0.15
P(CL-*co*-AVL)-**LD**-*g*-O3HT-**30**	0.249 ± 0.18
P(CL-*co*-AVL)-**HD**-*g*-O3HT-**30**	0.560 ± 0.33

Raman Spectroscopy



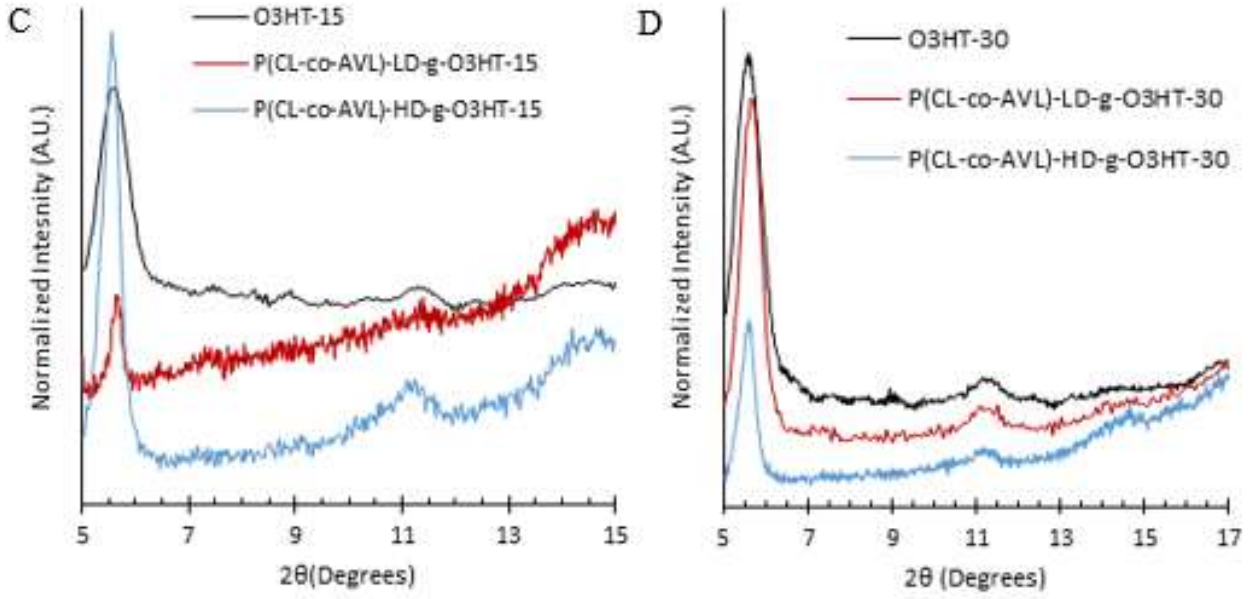
- Notable difference in sharpness of the peaks between O3HT-30 and O3HT-15, perhaps from higher degree of ordering.
- Shifting of the C=C (1449 cm^{-1}) stretching upon doping to form a new polaron peak (~1417 cm^{-1}).
- Sharper peaks in grafted samples compared to un-grafted samples, and bigger shift in peak energy.

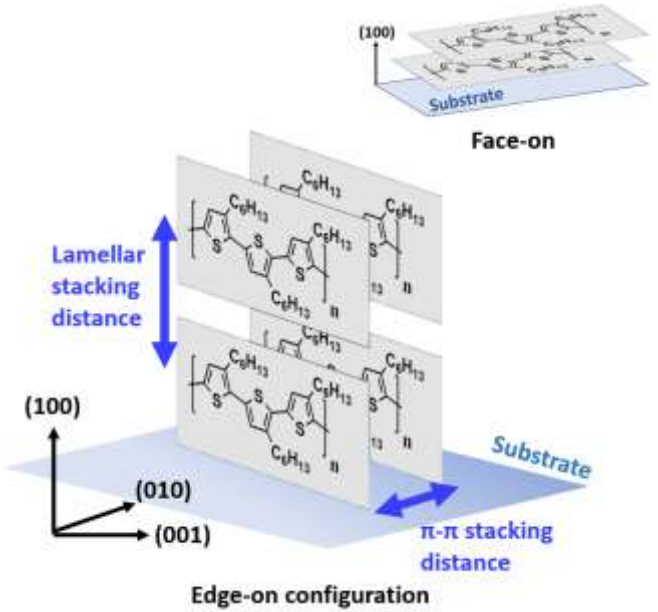
DSC Characterisation



- Crystallisation peaks in DSC that is not present in the “free” oligomer.
- Longer, grafted oligomers have higher degree of crystallization
- Higher density has lower crystallization temperature.

XRD Characterisation



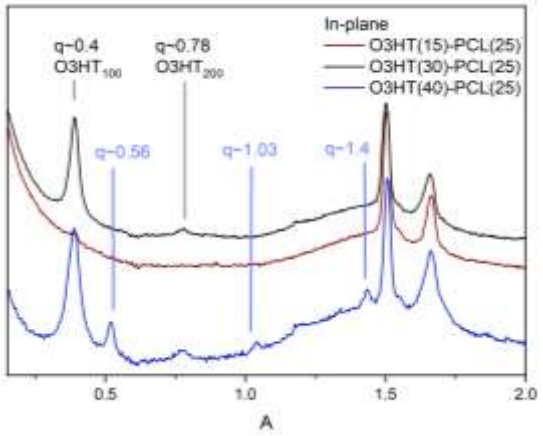


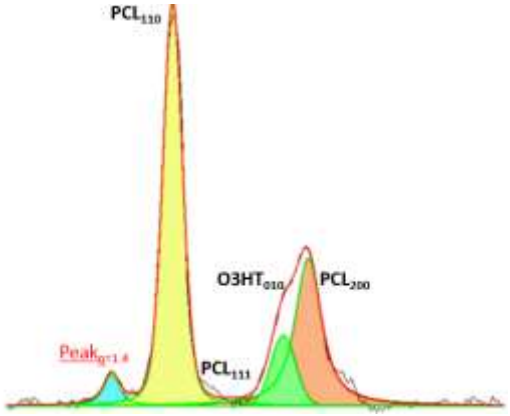
Phys. Chem. Chem. Phys. **2009**, *12* (1), 273–282.

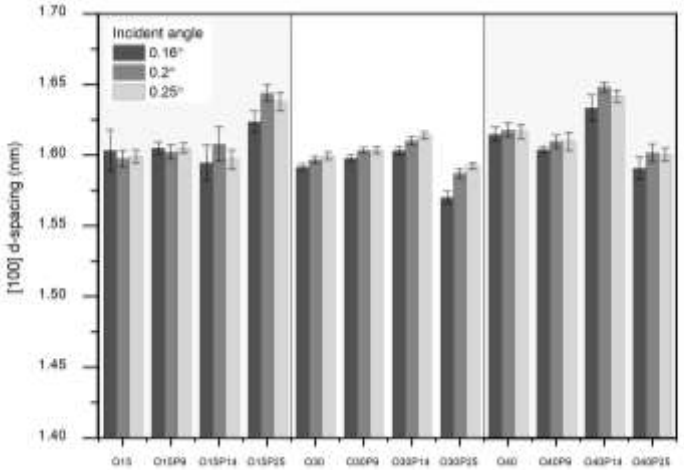
- XRD of films of P(CL-*co*-AVL)-*g*-O3HT
- Strong 2θ peak at 5.5°corresponding to 16 Å, consistent with the (0 0 1) Bragg peak of P3HT.
- (0 0 2) plane stronger in grafted samples and longer oligomers

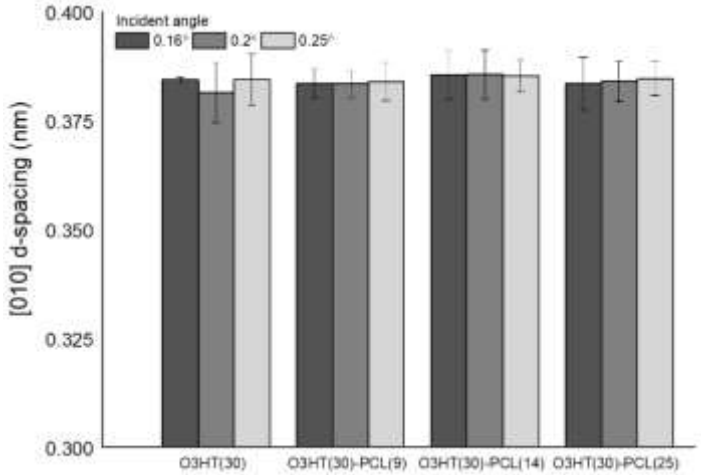
Yuhka Uda

Structural Relationship of Grafted O3HT and PCL and Effects of Additives and Annealing



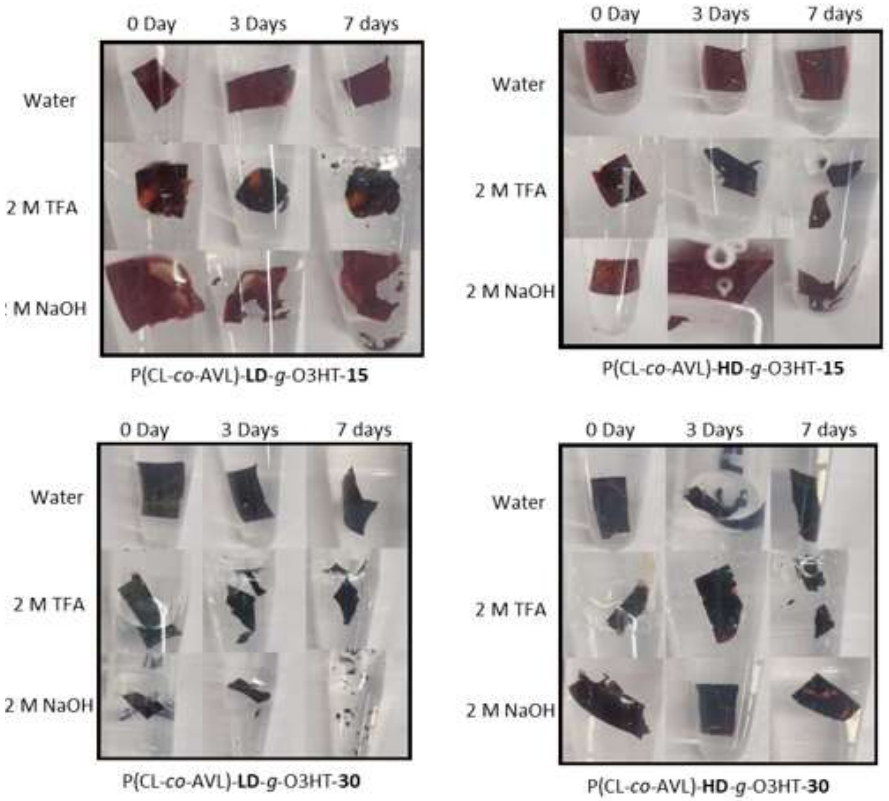




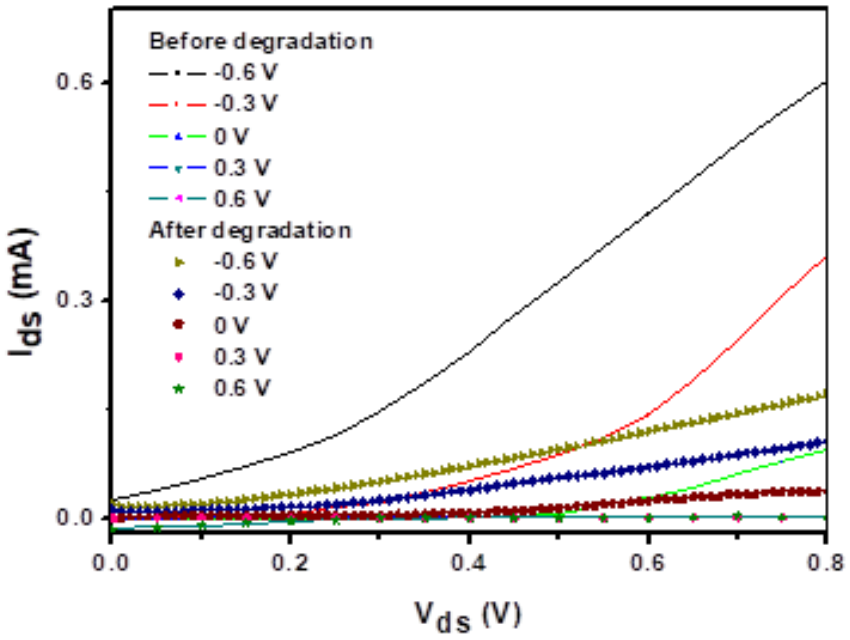


- Explored the configuration of P(O3HT-*g*-PCL) with different O3HT length, grafting density and treated with additives and/or annealing.
- Higher level of ordering with longer length, with annealing and additives also contributing the ordering.

Degradation and Device Performance



- Degradable in acidic and base, stable in water.
- Films of O3HT ungrafted does not degrade in the same solution.
- Films can be redissolved (after de-doping).



Dr. Bicheng (Amy) Zhu

- Transistor behaviour.
- On/Off state possible by applying different potentials to gate electrode.

Conclusion

- Synthesis of grafted co-polymer of O3HT and PCL derivative.
- P(O3HT-*g*-PCL) is electroactive and semi-conductive.
- Degradable and demonstrated in use as transistor.

Challenges/Future Work

- Grafting on other degradable polymers.
- More work on biocompatibility of degraded materials.
- Applications

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