Post-modification of butenolide polymers: Towards responsive polymers and coatings

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When designing new stimuli-responsive features in sustainable coatings, the responsive building blocks need to be compatible with green and naturally sourced monomers. One such recently developed sustainable monomer is based on the alkoxybutenolide scaffold, which is derived from biowaste, and can be functionalized through acetal groups[1]. In this work, a straightforward method for post-modification of butenolide copolymers is investigated *via* acid mediated boc-deprotection. Through post-modification of the deprotected polymers the desired functionalities can be incorporated. Incorporation of responsive units into such polymers will allow for controlling surface structure and properties of the coating.

Photo-oxidation of furfural

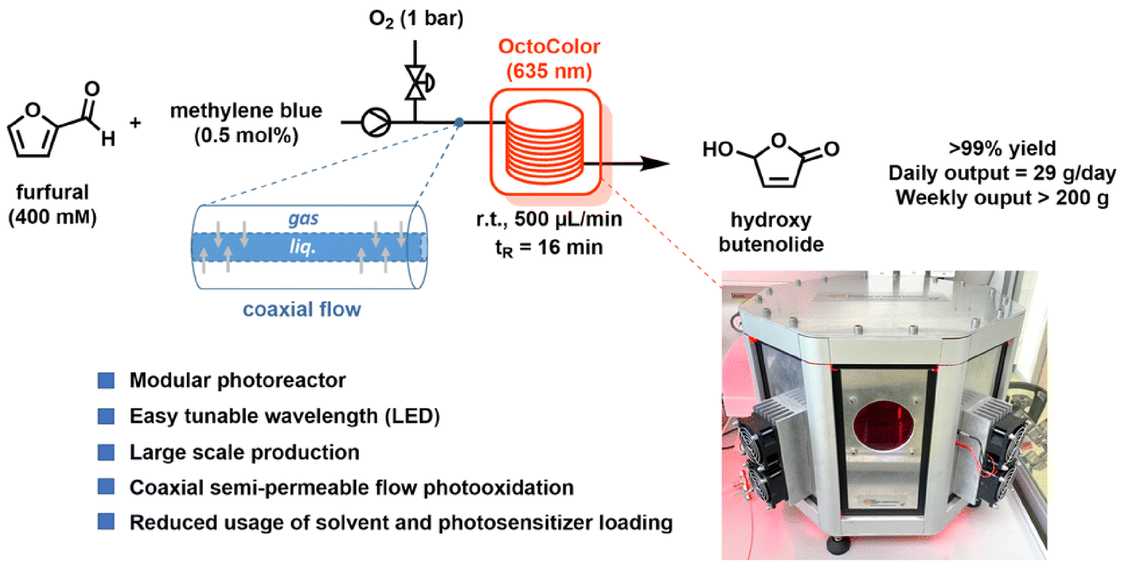


Figure 1: Continuous production of hydroxybutenolide from biowaste[2].

Polymerization of butenolides

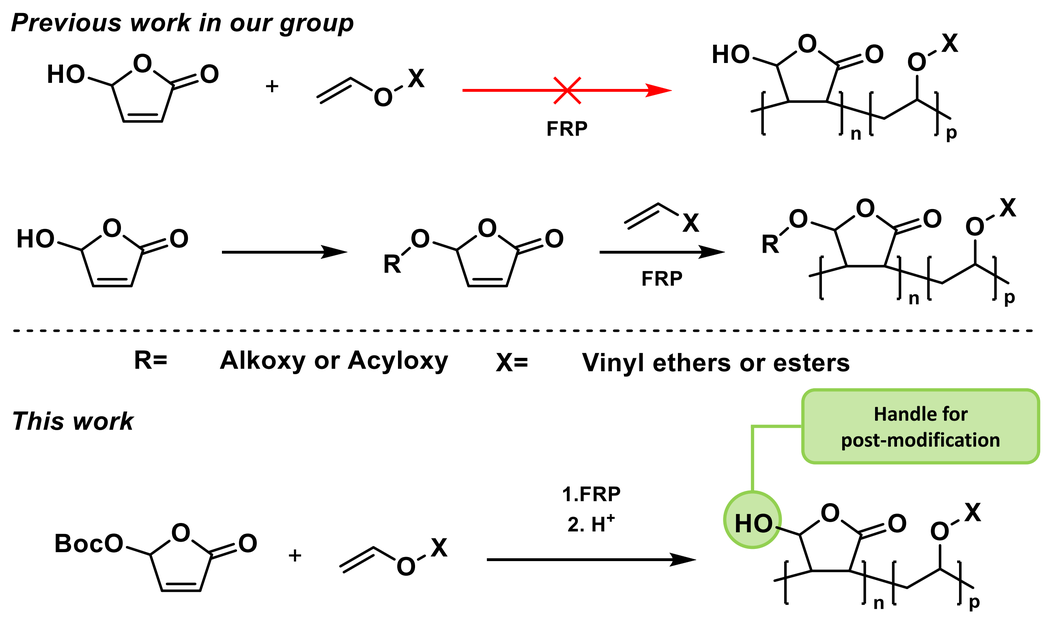


Figure 2: Polymerization of butenolides[1].

Post-modification *via* Boc-butenolide

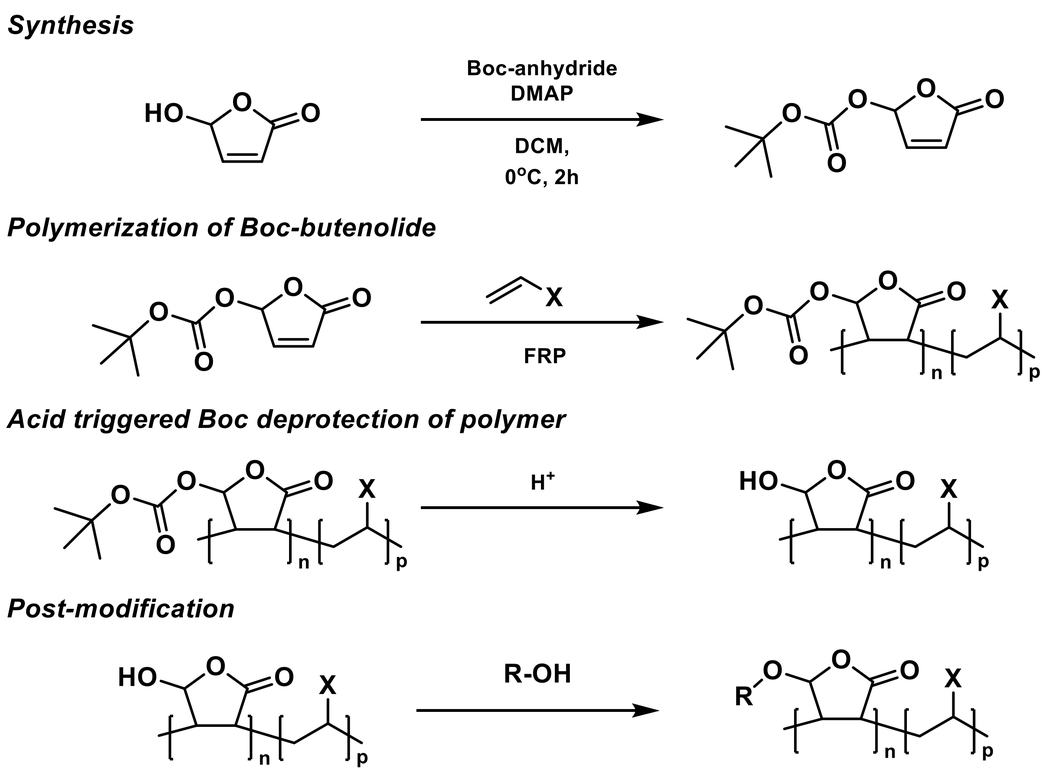


Figure 3: General route to functionalize butenolide copolymers[3].

Azobenzene-butenolide polymer films

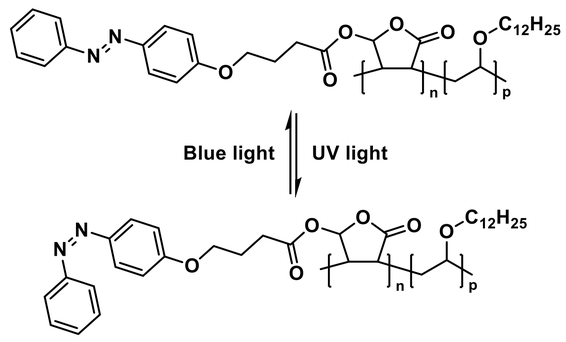


Figure 4: Azo-Polymer structure.

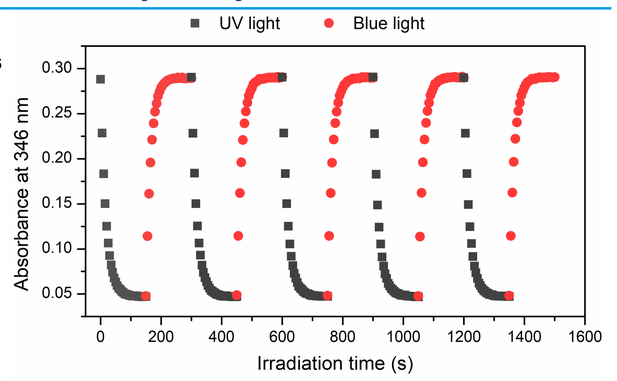


Figure 5: Photoswitching in polymer film

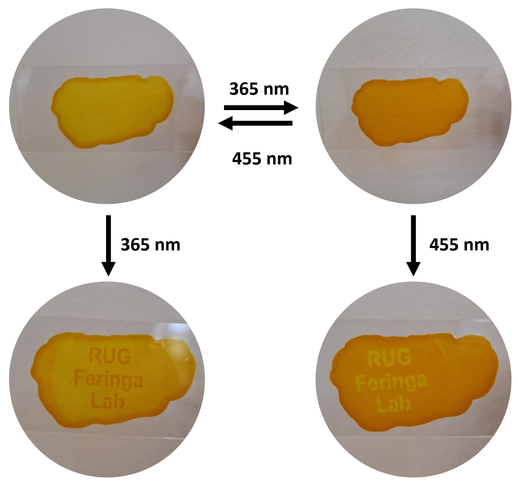


Figure 6: Color-changing polymer films.

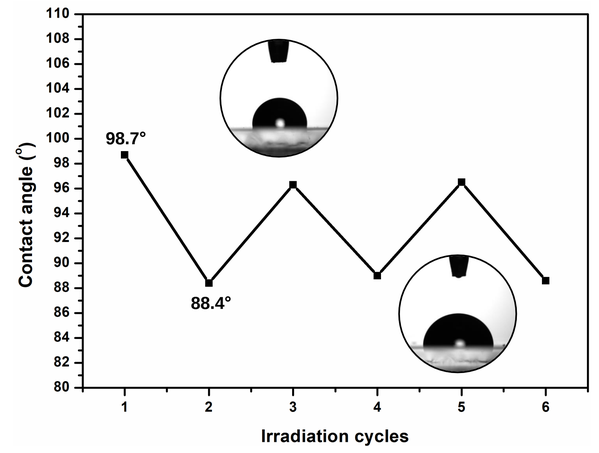
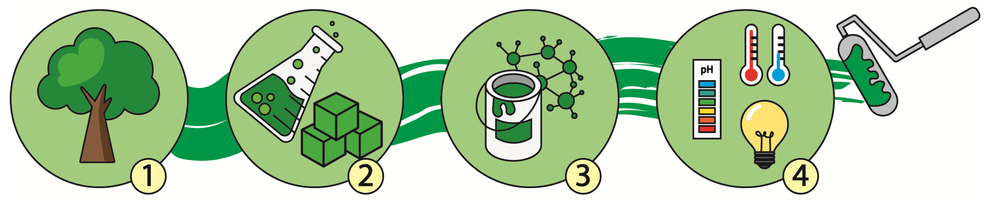


Figure 7: Switchable surface polarity.

Conclusion

- Post-modification offers a method to synthesize functional polymers inaccesible *via* direct polymerization.
- Introducing an acid-labile boc protecting group allows for efficient deprotection of the copolymers.
- Functionalization of the hemiacetal moiety to incorporate desired functionality.



References:

[1] Hermens, J. G. H., Freese, T., Van den Berg, K. J., Van Gemert, R., & Feringa, B. L. **2020**. *Sci. Adv.*, *6*(51), 26–42.

[2] Hermens, J. G. H., Lepage, M. L., Kloekhorst, A., Keller, E., Bloem, R., Meijer, M., & Feringa, B. L. **2022**. *React. Chem. & Eng.*, *7*(11), 2280–2284.

[3] Lepage, M. L., Alachouzos, G., Hermens, J. G. H., Elders, N., van den Berg, K. J., & Feringa, B. L. **2023**. *J Am. Chem. Soc.*, *145*(31), 17211–17219.

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