Synthesis of tunable and selectively degradable bis-phenol polymers

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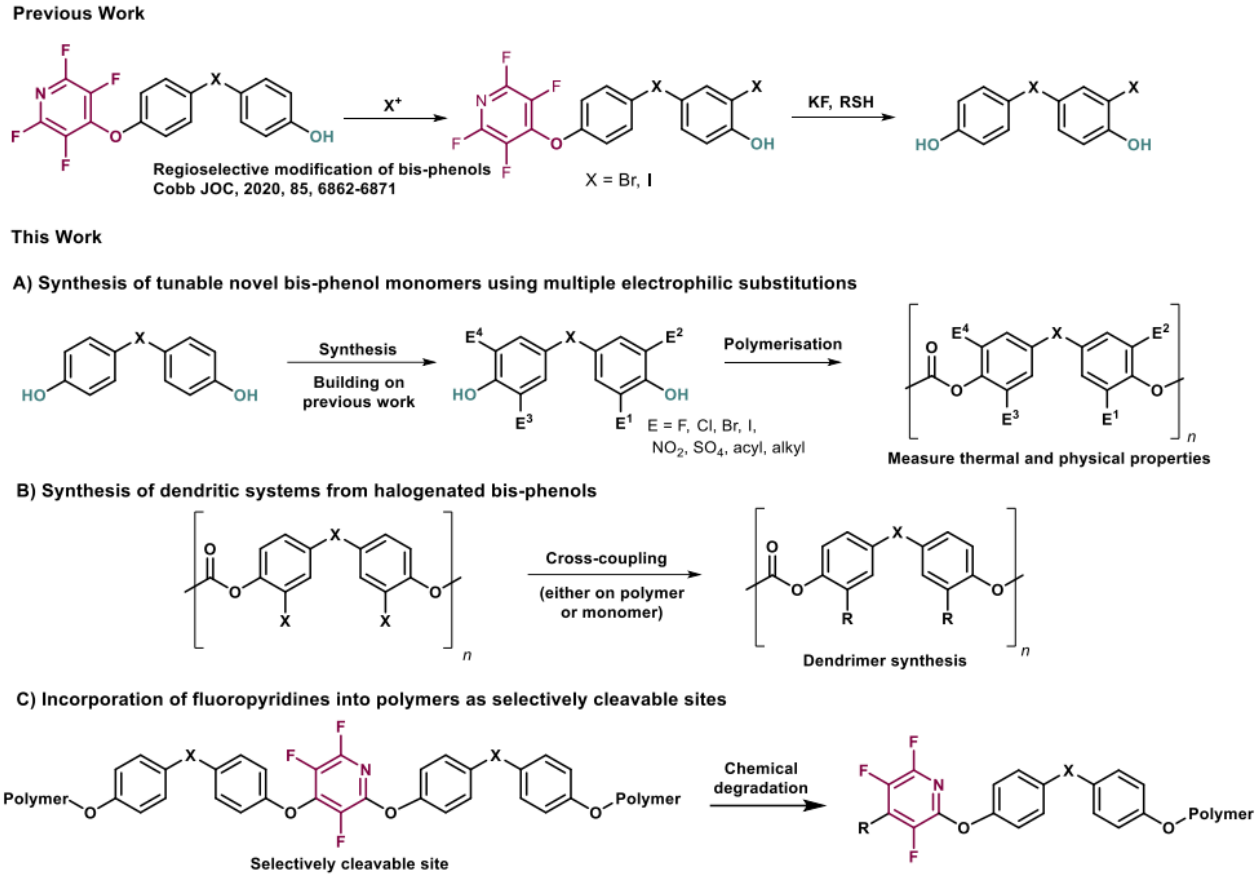
[3-month international - Professor Petr Beier at the Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences in Prague has agreed to be the host for the international student placement. Professor Beier is a world recognized expert in fluorine chemistry (handling and using elemental fluorine, F2), and specifically in the preparation of SF5 containing aromatics (https://beier.group.uochb.cz/en).]

This project will focus on the development of new tunable and selectively degradable bis-phenol based polymers. Plastics that use bis-phenol monomers (i.e. BPA) are ubiquitous; for example, they are common building blocks used in polycarbonates and epoxy resins. This has led them to be some of the most widely manufactured industrial plastics (the amount of BPA produced each year by 2023 is estimated to be 7,348 thousand tons)[1] and has seen them find use in everything from water bottles to bicycle helmets to rocket casings.[2] Despite their ubiquity, bis-phenol-based polymers have several drawbacks that have seen them become shunned for certain applications. BPA has been found to be an endocrine disruptor and there is a drive to remove it from products such as water bottles and food containers.[3] To tackle this problem new bis-phenolic monomers with varying properties are required. In addition, it has already been shown that modification of BPA can have significant impact on its properties; for example, polymerization of tetrabromo-BPA yields a highly heat-resistant polymer. [4] Therefore, the expansion of the bis-phenol monomer library is an exciting opportunity to find new applications and solve current problems.



Scheme 1) Project outline from building upon previous work to the synthesis of novel polymers and selectively cleavable sites.

Access to selectively modified bis-phenol monomers has been a longstanding stumbling block, especially given the identical electronic nature of the monomer's two phenolic rings. In 2020 the Cobb group published on the selective modification of bis-phenol systems and the regioselective electrophilic substitution of BPA

(Scheme 1). [5] This approach utilised a tetrafluoropyridyl protecting group to allow regioselective modification of bis-phenols with multiple electrophiles in a high-yielding and selective manner. This means that for the first time, it is now possible to both access these types of monomers but also be able to produce them on large enough scales to be viable for polymer synthesis. This project will exploit this methodology to access highly and selectively elaborated bis-phenolic monomers and produce novel polymers with tunable properties (Scheme 1A). Expanding upon the previously developed methodology, bis-phenolic monomers containing halogens, nitro groups, sulphate groups, acyl groups or alkyl chains will be synthesised (Scheme 1A). This will yield a library of diverse monomers with various physical and chemical properties which will then be polymerised via polycondensation. The polymers will be characterized using NMR spectroscopy, size-exclusion chromatography and light scattering studies. The polymers will then be tested for their physical, thermal and biological properties, and post-polymerisation modifications will also be attempted. For example, the incorporation of halogens into the polymer backbone gives a reactive handle for further transformations i.e. dendrimer synthesis through cross-coupling chemistries (Scheme 1B). Finally, the tetrafluoropyridyl group offers new avenues for selective degradation of bis-phenolic polymers (Scheme 1C). The Cobb group have previously shown that a fluoropyridine oxygen bond can be selectively cleaved under mild conditions.[6] By polymerisation through the fluoropyridine, cleavable sites will be introduced into polymers and their degradation properties established. This feature could effectively enable depolymerization on-demand, presenting a route to rapid polymer recycling.

References

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