Towards Degradable Poly(acrylic acid): Efficient Strategies for Hydrolyzable Breaking Points

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The persistence of hydrophilic polymers in wastewater streams is a growing problem, due to their abundant use in e.g. household products. They can enter the environment by being discarded on landfills through sewage sludge or incineration. Introducing easily fragmentable functional groups (breaking points) into their stable C-C backbone facilitates fragmentation into bio-assimilable, water soluble pieces in the disposal phase, while maintaining material stability during use. Poly(acrylic acid) (PAA) is the ideal candidate for this approach, as low molecular weight samples have been shown to exhibit significantly higher biodegradation rates compared to their high molecular weight counterparts. In our study, we incorporated cleavable ester groups into the C-C backbone of PAA *via* radical ring-opening polymerization of a cyclic ketene acetal.[1] These monomers enable polyester formation through a radical pathway. The copolymer was produced by copolymerizing *tert*-butyl acrylate and 2-methylene-1,3-dioxepane (MDO) and deprotected post polymerization. Direct copolymerization of MDO and acrylic acid is impossible due to a side reaction between the two monomers. We thoroughly investigated different polymerization methods. Deprotection was optimized to minimize chemical waste.[1] The poly(acrylic acid-co-ester)s degraded in KOH solution, leaving oligomeric fragments of PAA. These are easily assimilable for microbes. By preparing PAA-copolymer with hydrophobic MDO, maintaining water solubility is crucial for future applications. Hydrophilicity of the PAA-copolyesters was successfully maintained at higher pH levels for materials with a PAA content greater than 50%.[1]

Keywords: radical ring-opening polymerization, 2-methylene-1,3-dioxepane, acrylic acid, hydrolysis

References

[1] S. B. Däbritz, S. Agarwal, Evaluating Polymerization Methods and Deprotection Strategies for Making Water Soluble Poly(acrylic acid) with Hydrolyzable Breaking Points, *Macromol. Chem. Phys.* **2025**, 2500080.