

## Sustainable Polymers: Opportunities for the Next Decade

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**ABSTRACT:** The field of sustainable polymers is growing and evolving at unprecedented rates. Researchers are increasingly concerned with the feedstock origins and the degradation behavior of, especially, large-scale commodity packaging plastics. A perspective is offered here for the design of sustainable polymers, specifically addressing opportunities for monomer development and polymer degradation. Key concepts include: water degradability instead of biodegradability; incorporation of novel main-chain functionality, such as acetals; utilization of lignin-based aromatics; and direct polymerization of biogenic C1 feedstocks.



Paper or plastic? Polylactic acid (PLA) or polyethylene terephthalate (PET)? London or Paris? Which of these decisions impacts your sustainability index the most? An airline flight from Atlanta to Athens could include a layover in London or Paris. Paris lies closer to the Atlanta/Athens great circle and thus is the better option, resulting in a flight path of 5682 miles. Flying through London, however, would add 18 miles to your trip. This may seem inconsequential, but at 77 miles/gallon per passenger (typical for a Boeing 767),<sup>1</sup> this amounts to about 1.5 pounds of hydrocarbon fuel (per passenger), a mass equivalent to about 70 PET water bottles, a significant fraction of the 200 consumed annually per American. Now, what if you skip the journey to Athens altogether? That could save 500 pounds of fuel, or the mass equivalent of 23000 water bottles, just for one passenger!

The foregoing scenario paints a fairly bleak picture. When the average American consumes 21000 pounds of fossil fuel per year,<sup>2</sup> does it really matter if we save a few ounces or pounds by using biorenewable PLA instead of PET? The answer is complicated, but yes. First, small amounts of savings multiplied over large populations result in large savings. If each American used 100 instead of 200 bottles per year, then 30 billion bottles weighing 660 million pounds could be avoided. Second, a single 1/3 ounce bottle thrown onto the sidewalk ruins the landscape more visibly than the combustion products of the entire aforementioned intercontinental flight: 146000 pounds of fuel converted into 469000 pounds of carbon dioxide and 188000 pounds of water. While the byproducts of combustion are gaseous and invisible, the byproducts of the plastics industry are solid, visible, and usually quite persistent.

Where does all the plastic go? Recycling rates for PET are low in the United States (<30%) and invariably lower for other plastics. While some polymers are incinerated for energy production, most are discarded either to a landfill or directly into the open environment. Those plastics that float (principally polyethylene, polypropylene, and foamed poly-

styrene) have an easy route to the open ocean, the destination for an estimated 5 billion kg of plastic per year, equivalent to nearly 10000 kg per minute!<sup>3</sup> These startling numbers, combined with the deleterious effects of floating plastics on ocean ecosystems, have prompted the X Prize Foundation to develop the *Ocean Plastics X Prize*, to be awarded to a team that invents an environmentally safe, ocean-degradable alternative to petroleum plastics at a scalable volume.<sup>4</sup>

Scientific efforts toward the design, synthesis, and production of sustainable or *green* polymers have expanded tremendously in the last two decades. Of the 88 Presidential Green Chemistry Challenge winners since 1996, approximately 25% can be directly correlated to advances in sustainable monomers and polymers.<sup>5</sup> One of the most successful and visible is the NatureWorks process for the scalable production of polylactic acid from corn via fermentation technologies.<sup>6</sup> Twenty years ago, PLA was priced about 15–20 times more than PET and economic skepticism was plentiful. Today, the surcharge of PLA versus PET is only 15–25%, an amount small enough to allow its expansion into several packaging markets, including beverage cups dispensed at fast food restaurants. Despite the amazing and laudable efforts of NatureWorks, PLA suffers from some inherent drawbacks, including a low glass transition temperature (55–60 °C) and reliable degradability limited to stringent industrial composting conditions. Indeed, the pursuit of the *ideal sustainable polymer* continues.<sup>7</sup>

At the commercial forefront are several leading candidates, each with its own sustainability metrics.<sup>8</sup> For these, sugar is the most commonly employed feedstock. Sugar fermentation leads to the aforementioned PLA,<sup>9</sup> polyhydroxyalkanoates,<sup>10</sup> poly-(butylene succinate) (via biosuccinic acid),<sup>11</sup> biopolyethylene (via bioethanol),<sup>12</sup> biopolypropylene (via bioethanol),<sup>13</sup>

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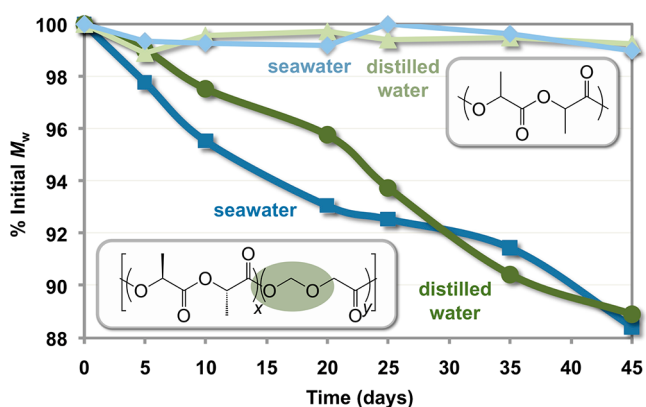
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biopolyvinyl chloride (via bioethanol),<sup>14</sup> polyethylene terephthalate (from bioethanol and conventional terephthalic acid),<sup>15</sup> and polypropylene terephthalate (e.g., Sorona, from bio-1,3-propanediol and conventional terephthalic acid).<sup>16</sup> Other promising commercial polymers include polycarbonates made from isosorbide (produced chemically from glucose)<sup>17</sup> or from the copolymerization of carbon dioxide and epoxides.<sup>18</sup>

Our research efforts have been strongly inspired by Nature. For example, the most abundantly created and degraded polymer on earth is cellulose, which harbors half of all organic carbon. Each monomer is connected by an acetal functional group, but this functionality is nearly absent in the commercial polymer repertoire (save for polyoxymethylene and polyvinyl butyral<sup>19</sup>).

We have incorporated the acetal functional group into the main chain of PLA, generating a family of polyesteracetal (PEA) copolymers, which are demonstrably susceptible to water degradation (Figure 1).<sup>20</sup> With 4 molar % of the acetal

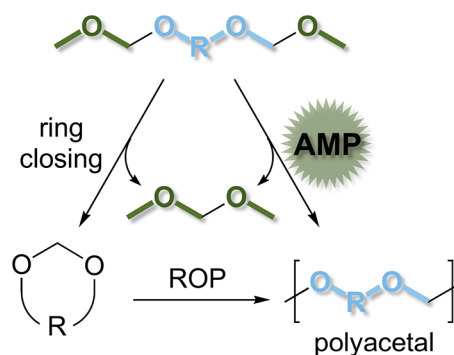


**Figure 1.** PLA copolymer with main-chain acetal functionality readily degrades in distilled water or seawater, as measured by a steady decrease in  $M_w$ . PLA is unaffected under these conditions.

unit present, the PEA steadily degrades in distilled water (pH = 7.0) or even slightly basic seawater (pH = 7.5). Extrapolated degradation times (based on mass-loss) are on the order of 5–10 years. Without this acetal unit, PLA is not water-degradable and must rely on enzymatic biodegradation,<sup>21</sup> which is typically absent in anoxic landfills or in cold ocean waters.

Our efforts to develop general synthetic strategies for polyacetals have focused on *Acetal Metathesis Polymerization* (AMP),<sup>22</sup> which is conceptually similar to acyclic diene metathesis (ADMET) polymerization.<sup>23</sup> Figure 2 depicts the polymerization of bis-acetals to yield polyacetals with the concomitant loss of a volatile acetal driving the step-growth polymerization to completion. Polydecylene acetal, for example, resembles polyethylene, but includes the hydrolyzable acetal functional group within the main-chain. Polymer melting temperatures are proportional to the methylene sequence length and values approaching those of polyethylene (130–135 °C) might be possible with methylene sequence lengths greater than 30. The best renewable source of long chain aliphatic diols seems to be bio-oils, and several research groups are pursuing such large monomers, which require C–C coupling chemistry to combine two fatty acids, because a single fatty acid is insufficiently long.<sup>24</sup>

We have extended this concept of functional group metathesis (FGM) polymerization to make polycarbonates (CaMP)<sup>25,26</sup> and polyoxalates (OMP),<sup>27</sup> in addition to the

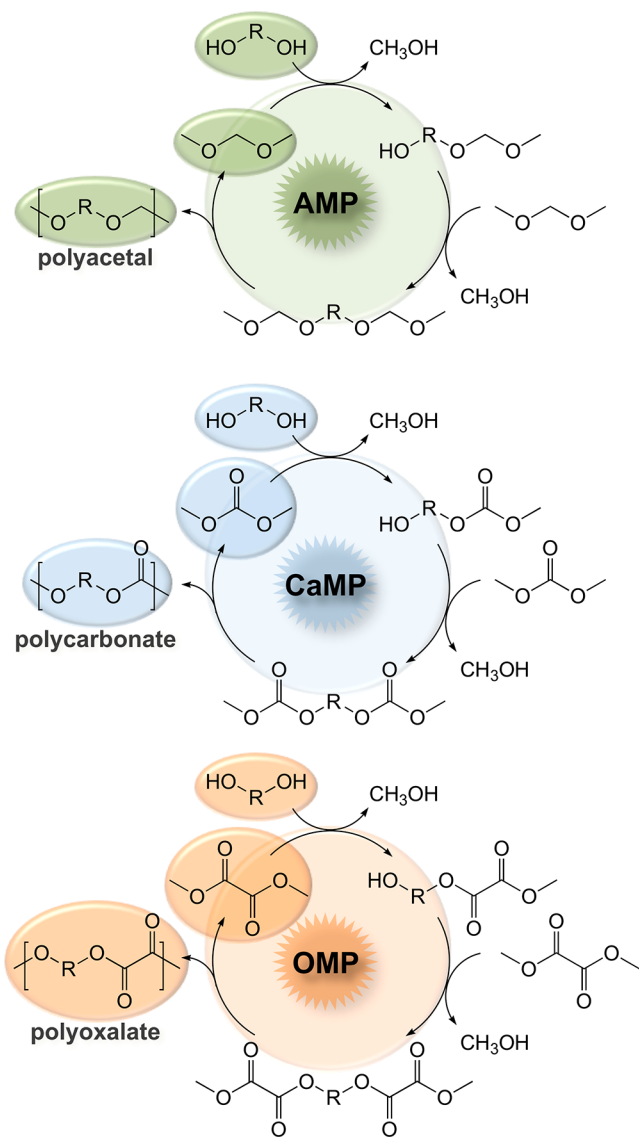


**Figure 2.** Acetal metathesis polymerization (AMP) affords a variety of polyacetals from bis-acetals and circumvents the preparation of cyclic acetals necessary for ring-opening polymerization (ROP).

aforementioned polyacetals. While the basic concept of FGM probably originated with Carothers around 1930,<sup>28</sup> our efforts have specifically targeted biorenewable feedstocks and have expanded the thermal temperature range of these polymer families. Moreover, judicious catalyst selection and reaction optimization have led to a direct method, which converts a diol and a small molecule directly to polymer, without the isolation of the bis-acetal, bis-carbonate, or bis-oxalate (Figure 3). Studies of the degradation behavior of our polyacetals, polycarbonates, and polyoxalates are ongoing but are quite promising in that water degradation generally occurs without a reliance on biodegradation. For example, over the course of 13 months, humid air alone apparently reduces the molecular weights of our polyoxalates by an order of magnitude.<sup>27</sup>

It might seem strange to focus on water degradation when water and water vapor are ubiquitous. An ideal time frame for polymer water degradation is around one decade. This is a compromise that exceeds the shelf life of most packaging products, but is 100 times shorter than the usual estimates for polyethylene degradation. Also note that the medical industry consumes large quantities of plastic, such as disposable syringes, that are hermetically packaged, employed for minutes, and then discarded. One company alone (Becton Dickinson) manufactures seven plastic syringes per person each year, amounting to over 100 million kg of PE per year. This is an ideal market for water-degradable polymers.

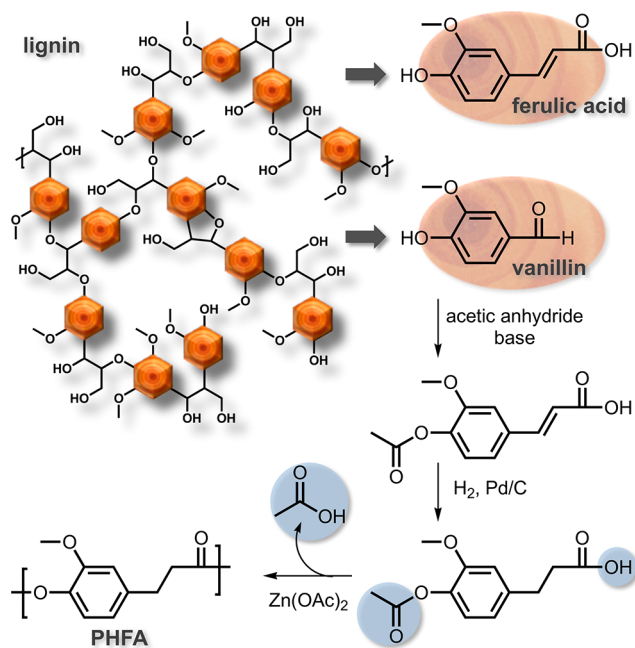
Despite the fact that lignin is the second most abundant polymer on earth (making up roughly 25% of vascular plants), there are no biogenic aromatic molecules produced on a large scale. Vanillin (from paper processing byproducts) and ferulic acid (from rice bran) are apparently the only two small-scale aromatic molecules harvested from lignin or lignocellulose. Employing these as feedstocks, we have created many polymers and copolymers with the objective of higher glass transition temperature thermoplastics, to improve upon PLA ( $T_g = 55$ – $60$  °C) and match or excel PET ( $T_g = 67$  °C).<sup>29,30</sup> An early patent success (1946) in this area copolymerized biobased furan dicarboxylic acid and ethylene glycol, resulting in a polyester with  $T_g = 86$  °C.<sup>31</sup> Our first successful PET mimic was polydihydroferulic acid (PHFA, Figure 4), which exhibited a desirable  $T_g$  of 73 °C and a  $T_m$  of 234 °C, which implies lower energy processing costs versus PET ( $T_m$  notably higher at 265 °C).<sup>29</sup> Copolymerization strategies have allowed refinement of the glass transition temperature, including a match of the  $T_g$  value for polystyrene (95–100 °C) en route to values exceeding 150 °C. Such thermal property control opens the door for use of these materials as polystyrene replacements and



**Figure 3.** Functional group metathesis (FGM) polymerization is amenable to the synthesis of polyacetals (AMP), polycarbonates (CaMP), and polyoxalates (OMP) directly from a diol and dimethoxymethane, dimethyl carbonate, or dimethyloxalate, respectively.

even higher temperature food packaging applications such as hot-fill bottling and canning processes. Moreover, the degradation products are biological antioxidants commonly found in tea, coffee, whole grains, and other antioxidant rich foods. In fact, ferulic acid itself is sold commercially as a dietary supplement in single tablet doses of 250 mg.<sup>32</sup>

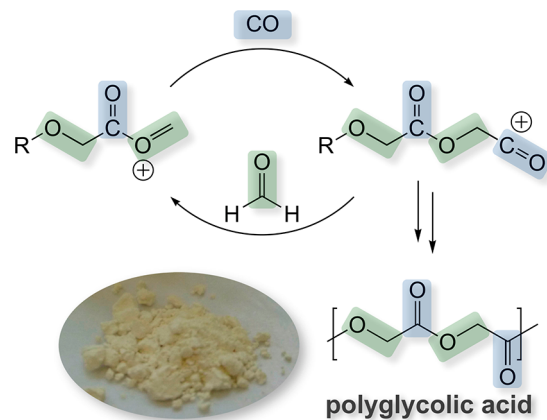
Ethylene is the most abundantly produced commercial organic molecule. Much of it goes into the 80 billion kg of polyethylene produced each year, which constitutes a 40% market share of all synthetic polymers. Because of increasing and tangible efforts to replace fossil fuels with sustainable biomass, it has been proclaimed that sugar is the new oil.<sup>33</sup> If that is the case, then a logical pondering is: "What is the new ethylene?" *Formaldehyde* is a tenable answer to this question. Formaldehyde and ethylene have nearly identical mass and both contain carbon participating in a reactive double bond, but formaldehyde also shares the oxidation state and empirical



**Figure 4.** Aromatics ferulic acid and vanillin are harvested from lignin and serve as feedstocks for high  $T_g$  and  $T_m$  polyesters, such as polydihydroferulic acid (PHFA;  $T_g = 73$  °C;  $T_m = 234$  °C).<sup>29</sup>

formula of cellulose and sugar (CH<sub>2</sub>O), which is approximately that of biomass.

One targeted application of formaldehyde is its perfectly alternating copolymerization with carbon monoxide, conceptually yielding polyglycolic acid (PGA). Reproduction of the conditions reported for this process 40 years ago<sup>34</sup> yields an amorphous, oligomeric, brown liquid. Eager to make crystalline, polymeric, colorless PGA, we optimized this reaction and obtained PGA that is functionally equivalent to commercial samples, but is made in fewer steps with significantly less generation of wasteful byproducts (Figure 5).<sup>35</sup> Note that



**Figure 5.** Cationic alternating copolymerization of C1 feedstocks formaldehyde and carbon monoxide affords polyglycolic acid (PGA).

Kureha America is the only company currently targeting PGA for packaging applications.<sup>36</sup> Their process hydrocarbonylates formaldehyde to yield glycolic acid, which is then conventionally polymerized via glycolide.

Cost and modest demand have heretofore thwarted the expansion of PGA into commercial packaging applications.

Importantly, the inexpensive C1 monomers formaldehyde and carbon monoxide are potentially made from methanol, which was a very sustainable/green monomer 100 years ago, as it was exclusively produced via the destructive distillation of wood (hence its common name of *wood alcohol*). A *Methanol Economy* has received serious consideration as a sustainable, biobased successor to the fossil fuel economy.<sup>37</sup> To the extent that the methanol economy expands in the future, polymers derived from this C1 feedstock will become economically privileged.

An impediment to the growth of green polymers is the daunting momentum of the existing fossil fuel-based polymer industry. The Chief Technology Officer of a Fortune 100 Company recently communicated that they are “highly interested in finding bio-based routes to [incumbent] commodity plastics which fit with current processing and disposal infrastructures,” but are “less concerned with developing new-to-the-world biodegradable plastics for our packaging and products.”<sup>38</sup> This mindset partly explains the success of biopolyethylene<sup>12,13</sup> and the PET PlantBottle,<sup>39</sup> along with the enormous interest in producing the 100% biorenewable PET PlantBottle 2.0.<sup>40</sup> Employing bioethanol from fermented sugarcane sugar, in 2010 Braskem first commercialized biopolyethylene, which is technically the capacity leader in biorenewable synthetic polymers.<sup>41</sup> Similarly, Coca-Cola has exploited bioethanol to synthesize the ethylene glycol comonomer of the PET PlantBottle, thus, achieving a 30% plant-based material. These approaches have nominally addressed the biorenewable challenge, but accomplish little with regards to the timely degradation of a polymer. Indeed, biopolyethylene and the PET PlantBottle possess the same woeful degradation behaviors as their fossil-fuel cognates. Akin to redirecting an oil tanker, the momentum of the \$400 billion/year packaging industry is changed fractionally and slowly. A quantum leap will likely occur only in response to considerable consumer demand coupled with a willingness to absorb the extra cost, at least during the introduction and growth phases of the next green polymer.

Over the next decade, sustainable polymer development will assuredly progress in several directions. Outlined here are several strategies that have been demonstrated yet retain considerable potential for future optimization: (1) synthesizing water-degradable polymers, containing, for example, the acetal functional group, that are not dependent upon narrow biological conditions for biodegradation; (2) installing specified functional groups into the polymeric main chain via functional group metathesis polymerization; (3) exploiting lignin-based aromatics for expanding the operative temperature range of green polymers; and (4) developing novel polymerization chemistry for utilizing abundant, inexpensive, and renewable C1 feedstocks. Consumer demand for functional and inexpensive green polymers is undoubtedly growing. Additional laboratory innovations will further facilitate our steady conversion from traditional polymers to sustainable and green polymers.

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### Notes

The authors declare no competing financial interest.

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