Isotactic Poly(propylene oxide): A Photodegradable Polymer with Strain Hardening Properties
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ABSTRACT: Leakage and accumulation of highly stable commercial plastics has led to substantial contamination of the environment. Highly isotactic poly(propylene oxide) (iPPO) was investigated as a potential high-strength thermoplastic with greater susceptibility toward degradation under ambient conditions. Various stereoregular forms of iPPO including enantiopure, enantioenriched, racemic, and stereoblock were synthesized with a single catalyst architecture in the presence of chain transfer agents. These materials were found to possess the same approximate ultimate tensile strength (UTS) via uniaxial tensile elongation (~75 MPa). A serrated tensile response corresponding to stress oscillations was observed in all forms of iPPO. An investigation on strain rate dependence showed that an increase in strain rate results in the decay and disappearance of the serrated response. Further evaluation of iPPO revealed its dramatic strain hardening afforded an UTS comparable to that of nylon-6,6. Exposing iPPO to UVA light (365 nm) resulted in photolytic degradation. Following 30 days of continuous exposure at 250 μW cm⁻², the Mₐ decreased from 93 kDa to 21 kDa, while samples not exposed to UVA light remained unchanged. Through selective stabilization with antioxidant additives, we believe iPPO could be a suitable replacement for nylon-6,6 in environmentally susceptible applications.

INTRODUCTION
As a consequence of global plastic production surpassing 350 million metric tons annually, plastic accumulation has become a substantial environmental crisis.¹ The Great Pacific Garbage Patch (GPGP), a 1.6 million square kilometer area between California and Hawaii, is estimated to contain over 79 thousand metric tons of plastic.² This garbage patch is but one of five major oceanic plastic accumulation zones and accounts for a small fraction of the estimated 4 to 12 million metric tons of plastic lost annually to marine environments.³ It was determined in 2015 that 52% of the total GPGP mass was composed of plastic fishing nets, ropes, and lines.⁴ These discarded materials not only contribute to garbage patch accumulation, but are the main contributor to “ghost fishing”, the unintended trapping and hindering of aquatic life. For products like synthetic fibers used in commercial fishing, efforts to reduce their eventual escape to the ocean are insufficient. While there is no panacea to persistent plastics, we sought to develop a polymer with the mechanical strength of an engineering plastic that also degrades under ambient environmental conditions (Scheme 1).

Isotactic polypropylene (iPP), high-density polyethylene (HDPE), and polyamides (PAs) are commercially used as synthetic fibers in marine applications.⁵ Although there have been significant efforts to develop degradation pathways for these materials, controlled degradation under ambient conditions has yet to be observed.⁶ The photodegradation of iPP and HDPE by ultraviolet (UV) light showed promise, but the low reactivity of the hydrocarbon backbone hinders the rate of degradation.⁶,⁷ While some commercial materials contain pro-oxidants to increase degradation susceptibility, their implementation has been discouraged due to facile initiation proceeding with negligible control and incomplete degradation.⁷ Guillet and Brubaker pioneered the development of UV-degradable ethylene—carbon monoxide copolymers.⁸⁻¹⁰ While further development of theses materials resulted in the commercialization and use in beverage can ring packaging, these materials lack the mechanical strength required for more
arduous applications such as commercial fishing. We sought to take advantage of the well-studied photodegradation of polyethers in designing a degradable polymer for higher strength applications.\textsuperscript{11–14} We rationalized that isotactic poly(propylene oxide) (iPPO) could be a suitable choice based on its structural similarity to IPP. Higher levels of tacticity in IPP increase its crystallinity, leading to enhanced mechanical strength, crucial for numerous applications.\textsuperscript{15} Achieving high tacticity in PPO could allow for similar mechanical properties to IPP while possessing ether linkages that are susceptible to photochemical degradation.

Although photodegradation provides a means of fragmenting polymer chains, it does not solve the polymer end of life problems. This fragmentation often leads to the formation of microplastics, persistent plastics on the micron scale.\textsuperscript{16} While the toxicological hazards of microplastics are not well understood, we believe iPPO is unlikely to persist as a microplastic due to additional degradation pathways. The amorphous analogue of iPPO, atactic poly(propylene oxide) (aPPO), also referred to as poly(propylene glycol), is often employed in environmentally susceptible applications.\textsuperscript{17,18} Several reports on the biodegradation of low molecular weight aPPO have revealed its low environmental persistence.\textsuperscript{19–23} aPPO can be metabolized by microorganisms under aerobic conditions through oxidation and cleavage in the alcohol and aldehyde dehydrogenase pathways.\textsuperscript{19} Following significant chain cleavage by UV light, we anticipate iPPO will be susceptible to the same biodegradation, albeit slower.\textsuperscript{24} While the biodegradation of iPPO is not included in this study, an active investigation is ongoing.

Commercial production of aPPO uses double metal cyanide catalysts in conjunction with alcohol chain transfer agents (CTAs) to produce low molecular weight polymers with narrow dispersities (\(D\)).\textsuperscript{25} Maintaining this control while achieving high levels of tacticity remains a challenge for the practical synthesis of iPPO. Enantioselective catalysts have been extensively studied for generating isotactic polyethers from racemic epoxides.\textsuperscript{26} This class of catalyst selectively polymerizes a single enantiomer while simultaneously resolving the less reactive epoxide. These systems have historically suffered from low selectivity, low activity, or a combination of the two, but significant progress in this area has recently been achieved.\textsuperscript{26–28} Our group has developed several generations of stereoselective Co and Cr catalysts with high levels of stereoselectivity (up to \([mM]\) > 99\%) and turnover frequencies of up to 5440 h\(^{-1}\) for PO polymerization.\textsuperscript{29–33} We have also reported the use of industrially relevant CTAs and chain shuttling agents (CSAs), which allow for precise control over the molecular weight at low catalyst loadings.\textsuperscript{34,35}

Highly isotactic PPO can be synthesized from enantiopure PO by a chain transfer polymerization (Scheme 2A). This synthesis requires a highly regioselective catalyst to ensure head-to-tail enchainment as well as enantiopure monomer, making it impracticable for large-scale production. Enantioselective chain transfer polymerization can also achieve highly isotactic polymer, where tacticity is dictated solely by the catalyst selectivity (Scheme 2B).\textsuperscript{26} Isoselective chain shuttling polymerization affords a unique polymer architecture in which both monomers are incorporated in a stereoblock (SB) configuration (Scheme 2C). To our knowledge, combining the bimetallic (salalen)/Cr(III) catalyst (rac)-1 with bis(triphenylphosphine)iminium chloride ([PPN]Cl) remains the only system reported to synthesize (SB)-iPPO.\textsuperscript{35}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme2.png}
\caption{Scheme 2. General Methods for iPPO Synthesis in the Presence of CTAs or CSAs}
\end{figure}

The moderate chain shuttling rate afforded by (rac)-1 and protic CSAs allows for the incorporation of large runs of a single enantiomer, preserving the high polymer isotacticity. Despite several methods of iPPO synthesis, little is known about the mechanical properties of this material. Herein, we report the synthesis of various stereoregular forms of highly isotactic iPPO and investigate their mechanical strength and photodegradation.

**RESULTS AND DISCUSSION**

In its enantiopure and racemic forms, complex 1 was used to polymerize enantiopure and racemic PO to generate each stereoregular configuration of iPPO (Table 1). Enantioenriched (S)-iPPO was afforded from (S)-1 and (rac)-PO in the presence of 1,6-hexanediol (1,6-HD) as a CTA (Table 1, entry 1). Its enantiopure form was synthesized from (S)-PO by (rac)-1 under similar reaction conditions (Table 1, entry 2). Enantiopure (R)-iPPO was generated in the same manner by using (R)-PO (Table 1, entry 3). (SB)-iPPO was synthesized from (rac)-PO using (rac)-1 in the presence of 1,6-HD as a CSA (Table 1, entry 4). Lastly, blending equal quantities of enantioenriched (S)- and (R)-iPPO in solution afforded highly isotactic (rac)-iPPO (Table 1, entry 5). Monomer and 1,6-HD loadings were modified to account for the number of initiating species to target a desired number average molecular weight (\(M_n\)). As intended, all synthesized forms of iPPO exhibit similar values of \(M_n\) and \(D\) (Table 1).

Each stereoregular form of iPPO was subjected to uniaxial tensile elongation following the removal of unreacted PO, 1, and dimethoxethane (DME) (Figure 1). Each material exhibited an elastic response until a sharp yield peak that was followed by a flat region and then an increase in stress until failure. As anticipated, enantiopure (S)- and (R)-iPPO exhibit the same tensile profile with an elastic modulus of ~290 MPa, yield stress of ~12 MPa, and ultimate tensile strength (UTS) of 75 MPa (Figure 1A). Although enantioenriched (S)-iPPO has minor errors due to some incorporation of (R)-PO (\([mM]\) = 96.9\%), its tensile response is indistinguishable from that of enantiopure (S)-iPPO (\([mM]\) > 99.0\%) at large strain (Figure 1B). It does present a somewhat reduced elastic modulus and yield stress of 248 and 11 MPa, respectively. (rac)-iPPO and (SB)-iPPO exhibited small losses (4 and 10
Table 1. Synthesis of Various Stereoregular Configurations of Highly Isotactic iPPO by 1 and 1,6-Hexanediol

<table>
<thead>
<tr>
<th>entry</th>
<th>polymer stereochemistry</th>
<th>PO 1</th>
<th>PO : 1,6-HD : 1</th>
<th>conv (%)</th>
<th>$M_n$ (kDa)</th>
<th>$M_n$ GPC (kDa)</th>
<th>$D$</th>
<th>$[mm]$ (%)</th>
<th>$T_m$ (°C)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>enantioenriched (S)</td>
<td>(rac)</td>
<td>32,000 : 15 : 1</td>
<td>61.5</td>
<td>71.8</td>
<td>104.0</td>
<td>2.68</td>
<td>96.9</td>
<td>66.1</td>
</tr>
<tr>
<td>2</td>
<td>enantiopure (S)</td>
<td>(S)</td>
<td>8000 : 5 : 1</td>
<td>98.7</td>
<td>83.9</td>
<td>97.2</td>
<td>2.23</td>
<td>&gt;99.0</td>
<td>68.4</td>
</tr>
<tr>
<td>3</td>
<td>enantiopure (R)</td>
<td>(R)</td>
<td>8000 : 5 : 1</td>
<td>98.4</td>
<td>83.5</td>
<td>99.4</td>
<td>2.37</td>
<td>&gt;99.0</td>
<td>68.6</td>
</tr>
<tr>
<td>4</td>
<td>stereoblock (SB)</td>
<td>(rac)</td>
<td>16,000 : 10 : 1</td>
<td>99.2</td>
<td>83.7</td>
<td>107.0</td>
<td>2.19</td>
<td>95.5</td>
<td>66.8</td>
</tr>
<tr>
<td>5</td>
<td>racemic (rac)</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

Polymization conditions: As specified above, [1] = 0.86 mM in DME, $1: [PPN]Cl = 1:2$, $T_{rxn} = 23 ^\circ C$, $t_{rxn} = 24$ h. Determined gravimetrically. Calculated using one polymer chain per compatible 1 and 1,6-HD (see Supporting Information eq S1). Determined by GPC in THF, calibrated with polystyrene standards. *Determined by $^{13}$C NMR spectroscopic analysis. Determined by differential scanning calorimetry (DSC). Reported values are from the second heat. ^1:1 solution blend by mass of entries 2 and 3 (n.a. = not applicable).

Figure 1. Representative stress–strain curves of various forms of iPPO strained at a rate of 100% strain min$^{-1}$. Traces separated for clarity: (A) enantiopure (R)- and (S)-iPPO (Table 1, entries 2 and 3), (B) enantioenriched and enantiopure (S)-iPPO (Table 1, entries 1 and 2), (C) (rac)-iPPO, (SB)-iPPO, and enantiopure (S)-iPPO (Table 1, entries 2, 4, and 5). X = sample fracture.

MPa, respectively) in UTS (Figure 1C). Interestingly, (rac)-iPPO had the largest elastic modulus (306 MPa) and yield stress (13 MPa) of these materials in conjunction with its lowest strain to failure. Upon first impression, it might be interpreted that the lower strength observed in (SB)-iPPO is the result of its lower isotacticy. However, its mm-triad content is similar to that of the enantioenriched (S)-iPPO (Table 1, entries 1 and 4), which exhibits the same tensile strength as enantioiure iPPO. The lower mm-triad content observed in (SB)-iPPO is intrinsic of its block microstructure. In contrast, the lower content for enantiopure (S)-iPPO is due to random incorporation of the less preferred enantiomer. As observed, a low percentage of random insertion errors have a negligible effect on the stress at break (Figure 1B), but the block microstructure does (Figure 1C). (SB)-iPPO maintains the approximate yield strength of all other forms of iPPO, but its tensile behavior diverges during strain hardening. Under continuous uniaxial elongation, semicrystalline polymer chains often realign after irreversible deformation enabling crystallization, otherwise termed as mechanical strain hardening. We attribute the lower UTS of (SB)-iPPO to inefficient chain alignment of the block architecture as it undergoes strain hardening.

We observed an unexpected serrated response during strain hardening (past ~100% strain) for all forms of iPPO (Figure 1). Control experiments with commercial iPP, HDPE, and nylon-6,6 resins confirmed this effect was a consequence of the intensive properties of iPPO and not the experimental setup (Figure S52). Although this behavior is more commonly observed in metals, stress oscillations (SOs) have been reported in a variety of common polymers such as HDPE, syndiotactic PP, polyethylene terephthalate, polynvinyl chloride, and bisphenol A polycarbonate.
mechanism for why SOs occur, a recent report by Hughes claims that the response is the result of crazing and formation of microcavities within their poly(butylene succinate) specimens.

Decades of investigation have shown SO dependence on temperature, strain rate, and the nature of the material. Due to the relatively low melting point of PPO (68 °C), the SO temperature dependence was not investigated. Instead, the SO strain rate dependence was monitored between 0.10% and 1000% strain min⁻¹ (Figure 2). When the strain rate was increased, there was a decrease in SO frequency. Increasing the strain rate above 100% strain min⁻¹ resulted in the decay and eventual disappearance of the serrated response, but caused a lower UTS. Tensile specimen shape was also found to affect the SO response (Figure S47). In an effort to report the most consistent UTS values, a strain rate of 100% strain min⁻¹ was used for all other mechanical testing experiments.

To determine the upper UTS limit of PPO, various molecular weights of enantioenriched (S)-iPPO were synthesized (Table 2). Enantioenriched (S)-iPPO was selected for this analysis as it provides the same mechanical strength as enantiopure polymer without the need for enantiopure PO. The Mn of iPPO can be controlled by adjusting the catalyst to monomer ratio, but changing the CTA loading provides the same effect without the need for higher catalyst loadings. Polymers were synthesized with Mn values ranging from 49 to 206 kDa. Each sample exhibited the same approximate tacticity, Đ, and yield strength (∼12 MPa). Mn values above 100 kDa resulted in negligible tensile improvement, as the 206, 130, and 104 kDa samples (Table 2, entries 1–3) exhibited similar UTSs (Figure 3). A small loss in tensile strength was observed when the Mn decreased below 104 kDa. Remarkably, the 49 kDa polymer (Table 2, entry 6) still produced an ultimate stress of 48 MPa.

With the upper UTS limit of iPPO identified, we performed a direct comparison to a few commercial plastics commonly used as high-strength synthetic fibers (iPP, HDPE, and nylon-6,6). Although iPPO exhibited a relatively low yield stress, its strain hardening resulted in an UTS that surpassed commercial polyolefins (Figure 4). Nylon-6,6 provided a much closer comparison, where the stress at break only differed by a few

Table 2. Synthesis of Enantioenriched (S)-iPPO with Varied Molecular Weight at Low Catalyst Loading

<table>
<thead>
<tr>
<th>entry</th>
<th>1,6-HD/(S)-1</th>
<th>Mn,exo (kDa)</th>
<th>Mn,GPC (kDa)</th>
<th>Đ</th>
<th>[mm] (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>182.0</td>
<td>206.0</td>
<td>2.24</td>
<td>96.4</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>109.0</td>
<td>130.0</td>
<td>2.90</td>
<td>97.9</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>76.0</td>
<td>104.0</td>
<td>2.68</td>
<td>96.9</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>52.6</td>
<td>86.4</td>
<td>2.36</td>
<td>95.6</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>36.3</td>
<td>60.5</td>
<td>2.32</td>
<td>96.0</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>27.2</td>
<td>48.9</td>
<td>2.31</td>
<td>96.2</td>
</tr>
</tbody>
</table>

Polymerization conditions: (rac)-PO:(S)-1:[PPN]Cl = 32 000:1:2, [(S)-1] = 0.86 mM in DME, T_rxn = 23 °C, t_rxn = 24 h. Calculated using one polymer chain per (S)-1 and 1,6-HD (see Supporting Information eq S1). Determined by GPC in THF, calibrated with polystyrene standards. Determined by 13C NMR spectroscopic analysis.
Notably, the elastic modulus of iPPO (∼275 MPa) is lower than both commercial polyolefins (iPP: 1200 MPa, HDPE: 1250 MPa) and nylon-6,6 (725 MPa). The immense strength resulting from the strain hardening of iPPO provides a material that rivals the strength of nylon-6,6.

With iPPO showing competency as a high-strength polymer, we decided to monitor its degradation under ambient conditions in the presence of UVA light. Solar UVA intensity varies dramatically based on location, season, and time of day. Typical mean daytime intensities for the United States are in the range 1050–2490 μW cm⁻². For this study, a less intense, but continuous and consistent exposure was implemented. A sample of enantioenriched (S)-iPPO was exposed to UVA light (365 nm) for 30 days at an intensity of 250 μW cm⁻². Degradation was monitored by gel permeation chromatography (GPC) to quantify the change in polymer Mn. Broadening of the dispersity was anticipated by random chain scission, but the high initial D value (>2.0) masked this effect. The exposed sample started to degrade in as little as 3 days, evident by a 9 kDa drop in Mn (Figure 5, blue). The Mn continued to decrease, resulting in a loss of 29 kDa over the first 15 days. A final measurement was collected after 30 days of continuous exposure, indicating the polymer Mn had decreased from 93 kDa to 21 kDa. Degradation of the same material in the absence of UVA light was also monitored (Figure 5, red). After the full 30 days, the Mn remained unchanged, consistent with no degradation.

In the interest of further understanding the degradation mechanism, enantioenriched (S)-iPPO was analyzed by NMR and IR spectroscopy after UVA exposure. ¹H NMR spectroscopic comparison with the products of thermally degraded aPPO characterized by Park and Heatley suggests that iPPO degrades via an autoxidation mechanism (Figure S53). Signals corresponding to the formation of formyl and acetyl end groups were observed in both degraded materials. IR spectroscopy supports these assignments with the notable appearance of a C=O absorbance at ∼1730 cm⁻¹ (Figure S54).

Small-molecule antioxidants are often employed as radical stabilizers in commercial polyethers and polyurethanes. Since radical sequestration is limited by stabilizer loading, polymer lifetime can be programmed to its application. Ongoing investigations aim to determine if the iPPO can be selectively stabilized by using commercial polymer additives.

**CONCLUSION**

In summary, iPPO has shown promise as a high-strength photodegradable polymer for applications at ambient conditions. While iPPO was synthesized in a variety of stereoregular forms, no substantial differences were observed in their tensile properties. Investigating the strength dependence on Mn revealed the upper UTS limit to be 75 MPa. The serrated response observed during strain hardening was a result of strain rate and intensive material properties. The robust strain hardening of this material generates an ultimate strength comparable to that of nylon-6,6. iPPO also showed photodegradation under continuous UVA exposure, reducing the Mn by 75% within 30 days. We believe that selective stabilization may be achieved by tailoring antioxidant loadings, allowing iPPO to serve as a nylon-6,6 replacement with limited environmental persistence.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c01768.

General experimental considerations, detailed procedures, material characterization, and additional supporting data (PDF)

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Notes

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