Poly(2,3-dihydrofuran): A strong, biorenewable, and degradable thermoplastic synthesized via room temperature cationic polymerization

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ABSTRACT: The creation of strong and tough plastics from sustainable and biorenewable resources is a significant challenge in polymer science. This challenge is further complicated when attempting to make these materials in an economically viable process, which is often hindered by the production and availability of chemical feedstocks as well as the efficiency of the monomer synthesis. Herein, we report the synthesis and characterization of a strong thermoplastic made from 2,3-dihydrofuran (DHF), a monomer made in one step from 1,4-butanediol, a bioalcohol already produced on plant scale. We developed a green, metal-free cationic polymerization to enable the production of poly(2,3-dihydrofuran) (PDHF) with molecular weights of up to 256 kg/mol at room temperature. Characterization of these polymers showed that PDHF possesses high tensile strength and toughness (70 and 14 MPa, respectively) comparable to commercial polycarbonate, high optical clarity, and good barrier properties to oxygen, carbon dioxide, and water. These properties make this material amenable to a variety of applications from food packaging to high strength windows. Importantly, we have also developed a facile oxidative degradation process of PDHF, providing an end-of-life solution for PDHF materials.

INTRODUCTION

The annual production of plastics exceeded 381 million metric tons in 2015.[1] With 90 % of polymers produced from petroleum feedstocks, plastics are projected to account for 20 % of annual petroleum consumption by 2050 without intervention. To reduce the carbon footprint and oil consumption of the plastics industry, there is a concerted effort to generate sustainable materials from biomass.[2] The exponential growth in global demand for poly(lactic acid) (PLA) illustrates the commercial interest in sustainable polymers; however, PLA can only meet a fraction of the total plastic demand due to brittle material properties, poor water barrier properties, and low heat stability.[3] In a recent review, Hillmyer and coworkers summarized three grand challenges of sustainable polymers: "The polymers of tomorrow should be derived from sustainable resources, should be highly effective in their intended use, and should offer sustainable solutions after use."[4] We envision that poly(2,3-dihydrofuran) (PDHF) can address these aims, where we hypothesize PDHF could be sourced from a commercial bioalcohol, provide a strong and tough thermoplastic, and degrade back to small molecules for biodegradation or chemical recycling (Figure 1).

Recent efforts to develop biorenewable polymers have focused on lactones, acrylates, and styrenic monomers derived from lignin.[5–7] While these monomers produce desirable materials, lignin valorization still faces many challenges in commercial development.[8] Carbohydrate-sourced monomers such as isosorbide and itaconic acid have also gained interest, offering a different biorenewable pathway.[9–11] However, isosorbide production is still inefficient, and generating desirable polymers from itaconic acid remains difficult.[12,13] Alternatively, bioalcohols represent a largely untapped resource in the production of biorenewable plastics. Several alcohols are already produced on plant scale from biomass for use as transportation fuel. In 2019 the United States produced 15.7 billion gallons of bio-ethanol and 1 million gallons of bio-isobutanol, and recently, Cargill announced plans to build a 65,000 ton per year plant dedicated to production of 1,4-butanediol from biomass.[14,15] In recognizing the facile methods available to transform biorenewable alcohols into vinyl ether monomers, we were inspired by the one-step cyclization of 1,4-butanediol to generate 2,3-dihydrofuran (DHF) developed by Leite and coworkers.[16,17] Based on our previous work in which we

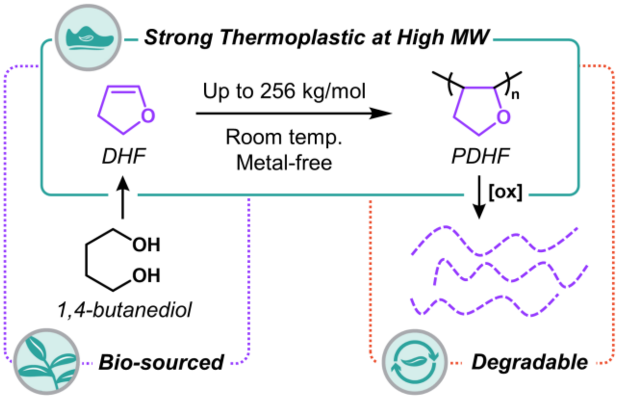

Figure 1: Poly(2,3-dihydrofuran) as a strong, tough, and degradable thermoplastic sourced sustainably from a bioalcohol.

incorporated this monomer as the glassy block of sustainable thermoplastic elastomers, we hypothesized that achieving high molecular weight (M_n) PDHF would produce a strong and tough thermoplastic.[18]

DHF has captured the interest of polymer chemists since the 1950s.[19] This cyclic vinyl ether results in a polymer with a restricted backbone, leading to a material with a high glass transition temperature of ~135 °C. Historically, the development of high T_g, sustainable polymers has been a grand challenge, where for example, much effort has been expended to increase the T_g of commercial plastics such as PLA (T_g ~ 60 °C) and polystyrene (T_g ~ 100 °C).[3,20] Higashimura and coworkers published the first controlled polymerization of DHF using iodine as an initiator at −40 °C.[21] Sanda and Matsumoto implemented a Lewis acid initiator to obtain a controlled polymerization at −78 °C and characterized the relationship between PDHF tacticity and T_g.[22,23] More recently, Aoshima and coworkers published a base-stabilized method that resulted in a controlled polymerization at 0 °C.[24] Tangentially, Xia and coworkers showed that ring opening metathesis polymerization (ROMP) of DHF produced a rubbery poly(enol ether) that could be depolymerized back to monomer or acid-degraded to small molecules.[25] Our previous report on reversible addition-fragmentation chain-transfer polymerization to generate PDHF and polyisobutyl vinyl ether block copolymers was performed at room temperature, and achieved only moderate PDHF molecular weights.[18] Overall, this extensive interest in DHF is underlined by the various patents issued for the synthesis and application of PDHF as a degradable fiber and thermoplastic.[26–34] Despite these many advances, all reported cationic polymerization methods require low temperatures and low monomer concentrations, resulting in substantial energy and solvent costs at plant scale. In addition to these drawbacks, only low molecular weight (M_n) PDHF has been produced, leaving the material properties of high M_n PDHF unknown. Thus, the development of an energy- and solvent-efficient controlled polymerization for high M_n PDHF remains a challenge.

Previous Lewis acid methods for controlled cationic polymerizations required low temperatures—likely to reduce reactivity and counteract exothermal heat generation and chain transfer.[21,24] This excessive chain transfer prohibits access to high M_n; thus, the development of a room temperature cationic polymerization to high M_n would represent a significant advancement. We recently demonstrated pentakis-(methoxycarbonyl)cyclopentadiene (PCCP) could initiate controlled polymerization of vinyl ethers under ambient conditions.[35] PCCP is a readily available, highly acidic reagent which provides a unique reactivity profile due to its extended carbanionic π-system. We hypothesized the strong coordination of the cyclopentadienyl anion to the propagating oxocarbenium chain-end directed monomer addition and prevented termination from adventitious nucleophiles while tempering the reactivity of the chain-end, allowing for room temperature polymerization. We posited that this new method could allow us to synthesize and characterize the properties of high M_n PDHF for the first time.

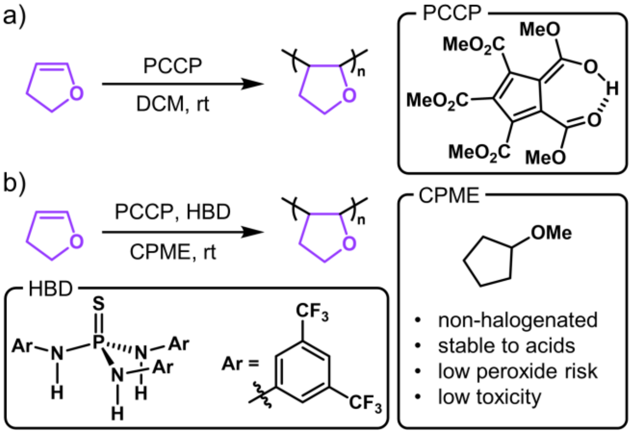

Figure 2: a) Controlled polymerization of 2,3-dihydrofuran using a metal-free, single-component, and room temperature method. b) Hydrogen bond donor (HBD) enables polymerization of DHF in the green solvent cyclopentyl methyl ether (CPME).

Herein, we disclose the metal-free, room temperature synthesis of high molecular weight PDHF (Figure 2a). Our polymerization method utilizes PCCP to target molecular weights from 20 to 250 kg/mol. Tensile characterization of PDHF demonstrated high ultimate tensile strength of up to 70 MPa, and high molecular weight samples achieved high toughness of up to 14 MPa. In addition, we produced optically transparent films with low gas and water permeability. As an end-of-life solution, we developed a facile degradation of PDHF under oxidizing conditions. This comprehensive study of PDHF provides a green method for the production of a strong and tough, high T_g thermoplastic from a readily available bioalcohol feedstock and provides an end-of-life strategy for this material.

RESULTS AND DISCUSSION

ROOM-TEMPERATURE POLYMERIZATION OF 2,3-DIHYDROFURAN

Our initial studies focused on the polymerization of DHF using PCCP as the initiator. Mixing PCCP and DHF in a 1:290 ratio in DCM resulted in 99 % conversion of the monomer after 2 h at room temperature to yield a 24.2 kg/mol polymer with a narrow dispersity ($Đ$) of 1.23 (Figure 3a, purple trace). Critically, the experimental (24 kg/mol) and theoretical (20.0 kg/mol) molar masses were in good agreement, suggesting that each PCCP led to a polymer chain and providing evidence that significant chain transfer was not occurring. By varying the ratio of the monomer to initiator we successfully targeted a wide range of molar masses up to 256 kg/mol (Table 1, entries 1-6). These high molar mass samples are an order of magnitude larger than what has been obtained by previous methods and, importantly, are still polymerized at room temperature. We found when targeting molecular weights above 100 kg/mol, the distributions did broaden slightly (Figure 3a); however, good agreement between theoretical and experimental M_ns were maintained.[†] Notably, this method was also amenable to large scale polymerizations, and we were able to successfully

Table 1: Controlled polymerization of DHF to high M_n using PCCP initiator.

Entry	[PCCP]:[DHF]:[HBD]	Solvent [e]	Time (h)	Conversion [f]	M_n^{theo} (kg/mol)	M_n^{exp} (kg/mol) [g]	Đ
1[a]	1:290:0	DCM	2	99%	20.0	24.2	1.23
2[a]	1:572:0	DCM	4	94%	37.6	37.9	1.27
3[a]	1:1420:0	DCM	17.5	99%	100	99.0	1.50
4[b]	1:2140:0	DCM	19.5	94%	142	140	1.51
5[b]	1:3570:0	DCM	26	99%	250	237	1.49
6[c]	1:3530:0	DCM	22	99%	248	256	1.62
7[d]	1:3570:0	CPME	168	39%	97.5	82.3	2.16
8[d]	1:3570:1	CPME	77	91%	229	214	1.42
9[d]	1:1427:1	CPME	23	96%	96.0	89.2	1.61
10[d]	1:713:1	CPME	3	85%	42.5	40.5	1.31

[a] 40 mmol DHF [b] 60 mmol DHF [c] 200 mmol DHF [d] 30 mmol DHF [e] [DHF] = 6.7M [f] Conversion calculated from ^{1}H NMR. [g] M_n and Đ determined by light scattering.

produce 250 kg/mol PDHF on a 14 g scale with an isolated yield of 95 % (Table 1, entry 6). Our initial results suggested that the polymerization of DHF was proceeding through a chain-growth process with living characteristics. To further support this suggestion, we monitored a polymerization by NMR and gel permeation chromatography (Figure 3b). As expected, we saw linear growth in the molar mass of the polymer relative to conversion. These initial results suggested that the polymerization of DHF was proceeding through a chain-growth process with living characteristics.

We next sought to improve the sustainability of our method by employing a green solvent in place of halogenated DCM. We have observed the solubility of PDHF in tetrahydrofuran (THF), but this is not an effective solvent for cationic polymerizations because it degrades by ring-opening under acidic conditions. In addition, THF readily forms peroxides which adds risk to large scale reactions. Cyclopentyl methyl ether (CPME) has recently captured attention in process chemistry as an alternative to THF and other ether solvents.[36,37] Watanabe and coworkers reported CPME does not readily form peroxides like other ethers and exhibits low toxicity.[38] In addition, its high boiling point and low energy of vaporization are favorable for solvent recovery. Because CPME has similar solubility properties to THF and is stable to acidic conditions, we hypothesized CPME would be an effective substitute for DCM.

We first attempted a polymerization targeting 250 kg/mol with our standard conditions in CPME. This reaction reached only 39 % conversion after 168 h, yielding an 82 kg/mol polymer with a broad dispersity of 2.16 (Table 1, entry 7). We attributed the slow rate of polymerization to the lower polarity of the solvent leading to a stronger interaction between the PCCP anion and polymer chain-end. To overcome this limitation, we took inspiration from our recent report that demonstrated the addition of a hydrogen bond doner catalyst, tris(3,5-bis(trifluoromethyl)phenyl) thiophosphotriamide (HBD), to increase the reaction rate of PCCP-promoted reactions and reduce chain transfer (Figure 2b). Addition of an equivalent of HBD relative to PCCP led to 91 % conversion after 77 h and yielded a 214 kg/mol PDHF sample with a narrow dispersity (Đ = 1.42) and good agreement between experimental and theoretical molar masses (Table 1, entry 8). We then extended this strategy to target various molar masses while maintaining excellent control over the polymerization (Table 1, entries 9 and 10). We propose that the HBD effectively weakens the association of the

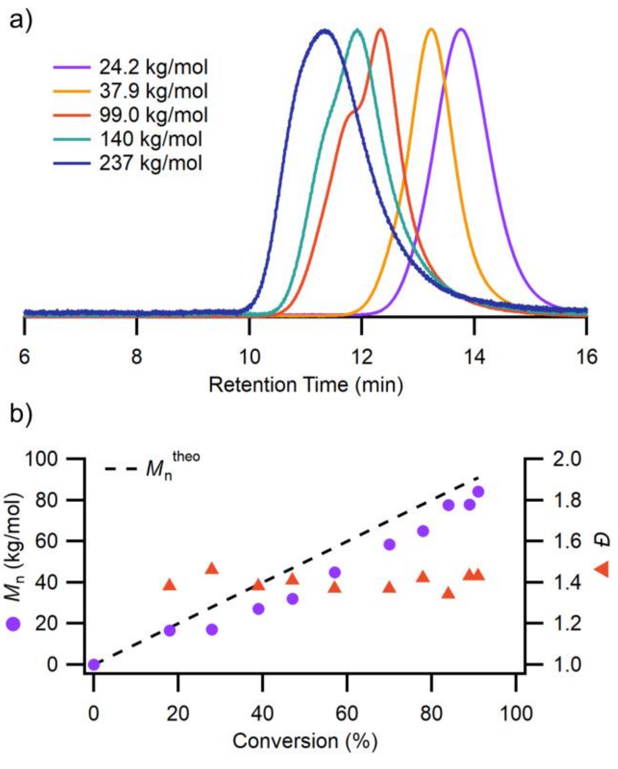

Figure 3: a) Gel permeation chromatography traces of PDHF targeting various M_n. b) M_n increases linearly with respect to DHF conversion.

Table 2: Tensile properties of PDHF at different M_n compared with polycarbonate.

Polymer-M_n	M_n [b] (kg/mol)	Đ [b]	Ultimate Tensile Strength (MPa) [c]	Strain at Break (%)	Toughness (MPa)
PDHF-53	53.4	1.45	69 ± 2	4.0 ± 0.2	1.6 ± 0.1
PDHF-78	78.0	1.50	70 ± 1	5.3 ± 0.2	2.5 ± 0.2
PDHF-140	140	1.51	65.9 ± 0.6	16 ± 2	6.1 ± 0.8
PDHF-198	198	1.47	65 ± 1	33 ± 14	14 ± 6
PC-45 [a]	45	N/A	62.8 ± 0.8	45 ± 19	22 ± 10

[a] Poly(bisphenol A carbonate) sample obtained from Millipore-Sigma. [b] Mn and Đ determined from light scattering. [c] Reported tensile data is the average of at least 3 samples.

PCCP anion with the oxocarbenium ion chain-end to enable the use of the less polar CPME solvent as a green alternative to DCM.

TENSILE PROPERTIES

We hypothesized that PDHF has not before seen widespread use because the low molar mass polymers which have been previously made led to brittle materials. We posited that by accessing higher molar mass samples of PDHF, we could increase the toughness and thus gain access to a material with highly desirable properties. Using the polymers synthesized with our new method (*vida supra*), we tested the tensile properties of PDHF samples with M_ns ranging from 53 – 198 kg/mol (Table 2 and Figure 4). Dogbone tensile bars were subjected to uniaxial tensile stress at a rate of 2 mm min^{-1}. All PDHF samples demonstrated high ultimate tensile strength (UTS), ranging from 65 to 70 MPa. Significantly, we found that high molecular weight samples exhibited a definitive yield event, or neck, and subsequent cold-drawing phase (Figure 4, *photo inset*). This drawing behavior dramatically increased strain-at-break up to 52 % (PDHF-198), which improved the toughness to a maximum of 14 MPa. Interestingly, strain hardening was not observed, and the polymer failed before full propagation of the neck through the entire gauge length. This behavior is indicative of unstable crazing leading to premature failure during the cold-drawing.[39–41] We hypothesize that the addition of plasticizing agents could stabilize this cold-drawing behavior and further improve both strain-at-break and toughness.

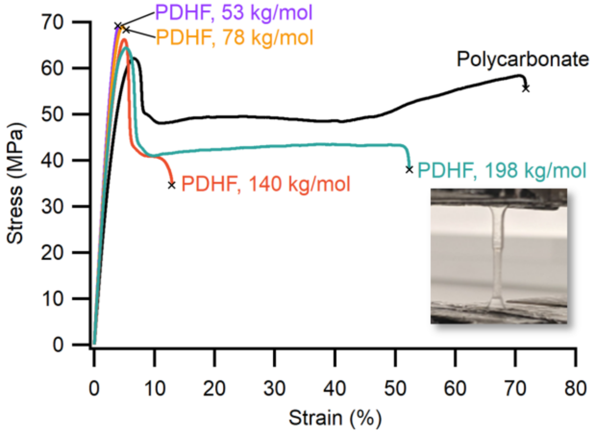

Figure 4: Stress-strain curves for PDHF samples compared to PC at a strain rate of 2 mm min^{-1} to failure, indicated by x.

Encouraged by the tensile properties displayed by PDHF-198, we compared it to a benchmark commercial polymer known for strength and toughness. Hence, a 45 kg/mol poly(bisphenol A carbonate) (PC-45) sample was prepared and tested under the same conditions (Figure 4, black trace). Notably, the yield strength of PDHF-198 was comparable to PC-45 (65 vs. 63 MPa, respectively). The strain-at-break for PC-45 exceeded that of PDHF-198 and the PC-45 sample underwent strain hardening, resulting in an overall tougher thermoplastic (22 vs. 14 MPa, respectively). The high strength and toughness of unformulated PDHF, as compared to PC-45, showcases its promise as a biorenewable engineering plastic.

THERMAL PROPERTIES AND RHEOLOGY

PDHF is unique as a poly(vinyl ether) due to the retained cyclic backbone structure giving the polymer a high glass transition temperature. We measured a T_g of 135 °C for PDHF, matching previous reports.[18,22] PDHF also has exceptional thermal stability, with a 5 % mass loss temperature of 364 °C. These thermal properties demonstrate a large processing window for PDHF, where heat molding and polymer melt processing can take place. Sanda and coworkers reported the influence of reaction temperature on the diastereoselectivity and consequently the T_g of PDHF.[22] Lower reaction temperatures favored the kinetic *cis*-isomer with a higher T_g while higher temperatures favored the thermodynamic *trans*-isomer with a lower T_g. Sanda's reported uncontrolled room temperature polymerization led to a low T_g of ~112 °C for the of 68 % *trans*-PDHF. In contrast, our controlled room temperature polymerization generated 65 % *trans*-PDHF with a high T_g of 131 °C for the same M_n (~30 kg/mol) (Table S2). We attribute this to the better control achieved in our polymerization and we believe the relationship between diastereoselectivity and T_g is more nuanced than previously reported. Consequently, our controlled polymerization provides access to high T_g PDHF at room temperature.

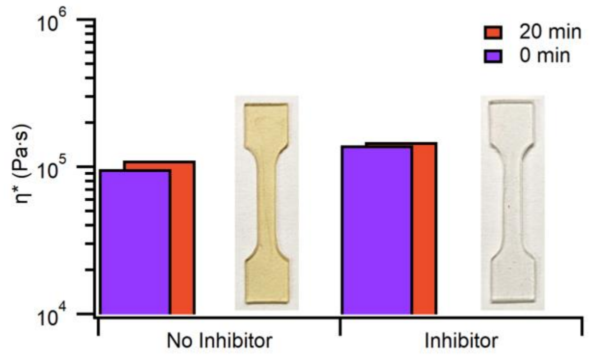

Figure 5: Melt stability of PDHF evaluated through complex viscosity (η*) monitored at 180 °C with 0.1 % oscillatory strain applied at a frequency of 0.1 rad s^{-1} for 20 min.

To evaluate the melt stability of PDHF, we subjected a batch of polymer to different processing conditions and evaluated the complex viscosity (η*) in parallel plate rheology. It was previously reported that PDHF is sensitive to thermo-oxidative degradation.[23] We hypothesized the addition of a commercial phenolic inhibitor (Irganox® 1010) would stabilize the polymer at elevated temperatures. PDHF samples from the same batch were prepared without inhibitor and with 0.07 wt % inhibitor. Constant 0.1 % oscillatory strain was applied at a frequency of 0.1 rad s^{-1} for 20 minutes at 180 °C. Uninhibited PDHF showed a greater increase in η* over 20 minutes when compared to the inhibited PDHF (Figure 5). In addition, uninhibited samples would often turn yellow during heat molding, while inhibited samples remained clear. This provided discernible evidence that the inhibitor increased the thermal stability of PDHF.

Another key parameter that influences polymer properties is the entanglement molecular weight (M_e). Using time-temperature superposition to generate a master curve, the M_e was calculated to be ~3 kg/mol using the equation given by Ferry (Figure S14, Equation S1).[42,43] In reference to other polymers, this is quite low; for example, the value for polystyrene is estimated to be 18 kg/mol.[43] Generally, a low M_e is associated with a strong thermoplastic, such as observed with PC (M_e = 2.5 kg/mol).[44] Consequently, we believe PDHF derives its strength from being well entangled, where $M_n >> M_e$. In addition, because PDHF is amorphous with a high T_g, it should maintain melt strength making it amenable to extrusion and other polymer processing techniques where high melt viscosity at low frequencies is desirable.

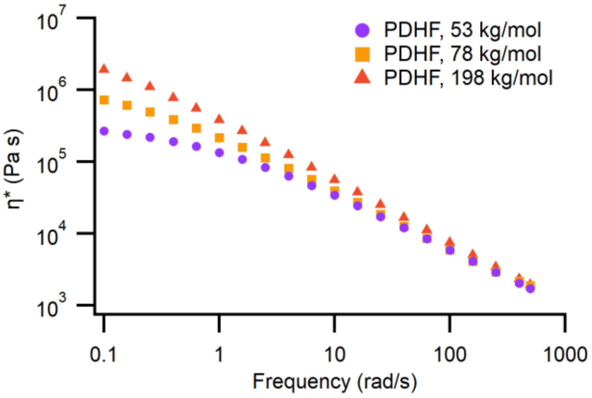

Figure 6: Frequency sweeps of PDHF-52, PDHF-84, and PDHF-198 showing the effect of M_n on complex viscosity (η*).

The influence of M_n on melt properties was then examined with frequency sweeps performed at 170 °C from 0.1 to 100 rad s^{-1}. Storage (G') and loss (G") moduli showed a clear crossover frequency that shifted to lower frequencies with increased M_n (Figure S15). The crossover between G' and G" indicates the frequency at which the polymer transitions from fluid-like to solid-like, giving insight into the sheer rates needed for melt-processing.[45] The plot of η* at 180 °C shows an increase in η* with respect to increasing M_n at low frequency (<0.1 rad s^{-1}), indicative of the increased zero-shear viscosity (Figure 6). Above 100 rad s^{-1} the η* for all samples converge as a result of shear thinning.[46] The onset of shear thinning indicates the shear rate at which viscosity diminishes with increased frequency, an important consideration in many polymer processing techniques, allowing PDHF of varying molecular weight to be processed with similar η* above 10 rad/sec .[46] Finally, the range of observed complex viscosities suggests that PDHF could be well suited for hot-melt extrusion processing, as the optimal viscosity range has been cited as 1000–10000 Pa·s.[47]

FILM BARRIER PROPERTIES

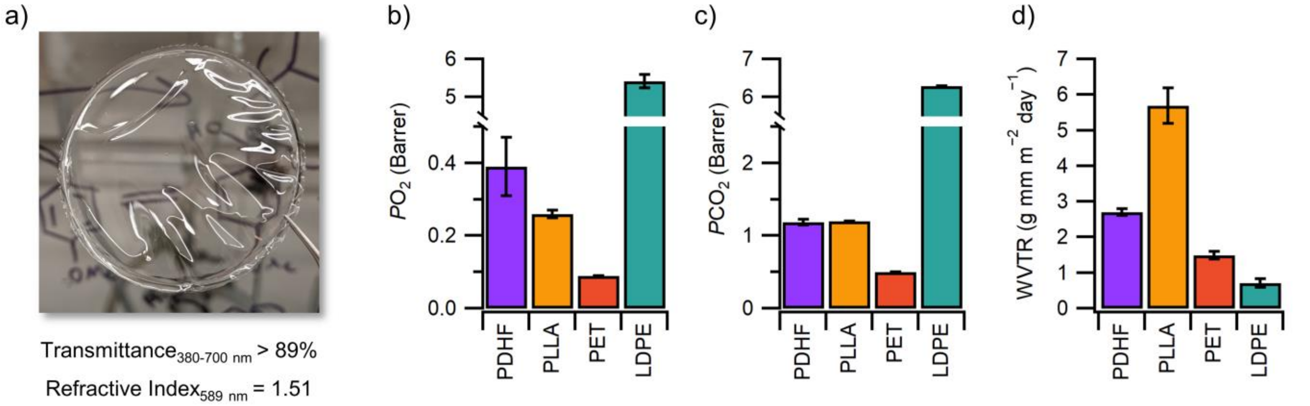

Figure 7: PDHF films demonstrate desirable optical properties (a) and moderate permeability for O$_2$ (b), CO$_2$ (c), and water vapor (d).

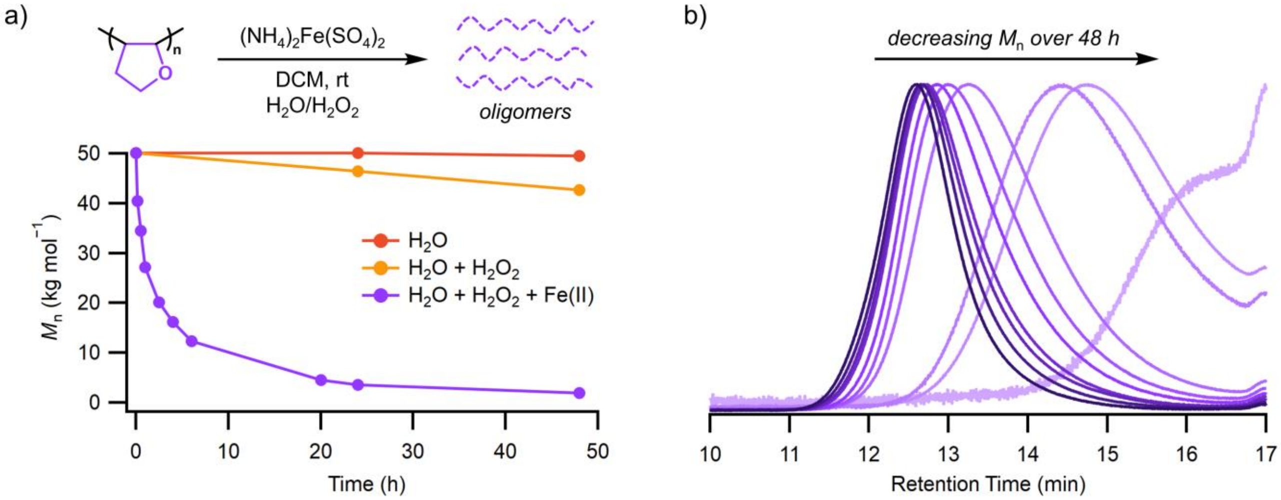

Figure 8: a) Facile oxidative degradation of PDHF using Fenton's reagent (Fe(II)/H_2O_2) reduced the polymer to oligomers over 48 hours. b) Gel permeation chromatography traces show a clear decrease in molecular weight.

To study how PDHF may perform as a barrier material for food packaging applications, we produced free standing films for analysis. These films were solvent cast then pressed at 170 °C to ensure the polymer was thermally relaxed. This produced uniform films ~38 μm thick with > 89 % transmittance across visible wavelengths (380-700 nm) (Figure 7a). For gas permeation measurements, PDHF films were tested by introducing an upstream pressure (1-17 atm) of single gas penetrants (O_2 or CO_2) and measuring downstream pressure.[48–50] Water vapor transmission rate (WVTR) was tested using previously described methods, in accordance with ASTM-E96.[51–53] The values recorded for PDHF were compared to data from a recent publication on sustainable packaging materials (Figure 7b-c).[54] Previously, high strength thermoplastics such as PC have had poor barrier properties, therefore, we wished to compare PDHF to materials currently used in barrier applications. O_2 permeability (PO_2) for PDHF at was lower than LDPE, but higher than PLLA and PET. CO_2 permeability (PCO_2) for PDHF was again lower than LDPE, and comparable to PLLA, but not as low as PET. Measured values for PDHF WVTR were low, at 2.7 g mm m^{-2} day^{-1}. This is comparable to PET, (1.49 g mm m^{-2} day^{-1}) and a significant improvement over PLLA (5.7 g mm m^{-2} day^{-1}). The lower WVTR and resistance to hydrolysis gives PDHF clear advantages over PLLA for water-exposed applications. PDHF combines moderate gas and water permeability with robust material properties to produce a biorenewable polymer that could be attractive for food packaging applications.

ACCELERATED OXIDATIVE DEGRADATION OF PDHF

In the development phase of any new plastic, it is imperative to examine the end-of-life solutions available for recycling and/or degradation. PDHF with inhibitor is a stable thermoplastic and thus can be mechanically recycled. However, we also wanted to investigate the chemical degradation of this material. Early work by Sanda and Matsumoto demonstrated the slow degradation of PDHF in the presence of air and proposed an oxidative chain scission mechanism.[23] They reported a reduction in M_n from 85 to 4.5 kg/mol occurred after an uninhibited, high surface area sample was exposed to air for 130 days at room temperature. Motivated by this work, we sought to develop a method by which we could chemically accelerate PDHF degradation to oligomeric and small molecule fragments, which may hold potential for more favorable biodegradation or for waste valorization through chemical upcycling.

It is well known that the combination of hydrogen peroxide (H_2O_2) and a ferrous salt (Fe(II)), "Fenton's reagent," results in the formation of a strongly oxidizing hydroxyl radical species.[55] Due to the relative abundance and low cost of H_2O_2 and Fe(II), we sought to use a Fenton's reagent oxidation to demonstrate a facile, accelerated chemical degradation of PDHF. PDHF was first dissolved in DCM before adding H_2O_2/H_2O (30 wt %) and Fe(II) in the form of $(NH_4)_2Fe(SO_4)_2{\bullet}6H_2O$. DCM was chosen because it met our criteria of being difficult to oxidize while still providing good solubility for efficient degradation. On larger scale, 1,2-dichloroethane could serve as an alternative, where the solvent could be recovered and recycled. The biphasic reaction mixture was then monitored by GPC, revealing a reduction in M_n from 50 kg/mol to ~1 kg/mol over 48 h (Figure 8). The plot of M_n^{-1} versus time exhibited a linear relationship, suggesting a chain scission mechanism (Figure S22). When PDHF was stirred in only water and DCM, no reduction in M_n was observed, and when PDHF was stirred in H_2O_2, H_2O, and DCM but no Fe(II), the M_n only decreased to 42.7 kg/mol after 48 hours. These results demonstrate Fenton's reagent as an effective method for the rapid, facile degradation of PDHF.

^1H NMR, ^{13}C NMR, and FT-IR spectra of the degradation products provided initial insight into the mechanism. By ^1H NMR (Figure S23), we observed signals consistent with a carboxylic acid (10.70 ppm), aldehyde (9.11 ppm), as well as an acetal (5.43 ppm), and in the ^{13}C NMR spectrum (Figure S24), a peak consistent with that of a lactone (162.07 ppm) was visible. These assignments were supported by FT-IR spectra (Figure S25), in which new absorptions for

C=O stretching were observed at 1730 and 1770 cm^{-1} in addition to a broad absorption ranging from 3050 to 3500 cm^{-1} corresponding to O-H stretching. These observations align with those made previously for PDHF degradation, and we expect that our accelerated oxidation proceeds through a similar mechanism (Figure S26).[23] This degradation study sets the groundwork for the development of a method to chemically upcycle PDHF, where optimization could allow for complete valorization of the oligomeric products into chemical feedstocks.

CONCLUSIONS

PDHF represents a unique opportunity to source a strong and degradable thermoplastic from a commercial bioalcohol. We demonstrated that PCCP is an effective organic acid initiator for cationic polymerization of DHF at room temperature to achieve high M_n PDHF (256 kg/mol) at 14 g scale. The addition of HBD enabled polymerization in an industrially relevant green solvent, CPME. Tensile properties revealed that high M_n PDHF is a strong (≤ 70 MPa) and tough (≤ 14 MPa) thermoplastic, comparable to PC. Film barrier properties showed promising results for food packaging, with low permeability to O_2 (0.42 barrer), CO_2 (1.2 barrer), and water vapor (2.7 g mm m^{-2} day^{-1}). Finally, we demonstrated an accelerated chemical degradation of PDHF under oxidizing conditions. This comprehensive evaluation of PDHF lays a roadmap for developing this next-generation sustainable thermoplastic, where we have provided an efficient bioalcohol source, robust material properties, and facile degradability.

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† We discuss a possible chain-transfer and chain-coupling mechanism in the Supporting Information.

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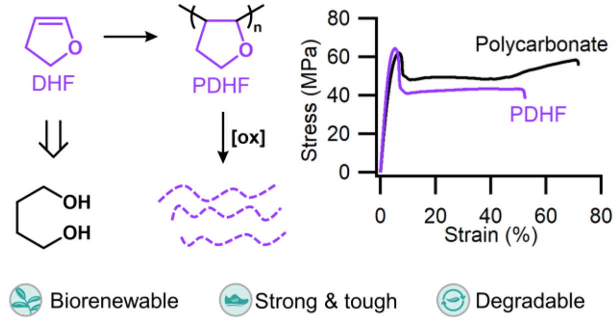
TOC Graphic:



DHF
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PDHF
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OH
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40
20
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Stress (MPa)
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80
Strain (%)
Polycarbonate
PDHF
Biorenewable
Strong & tough
Degradable