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Biomass-Derived Degradable Polymers via Alternating Ring-Opening Metathesis Polymerization of Exo-Oxanorbornenes and Cyclic Enol Ethers

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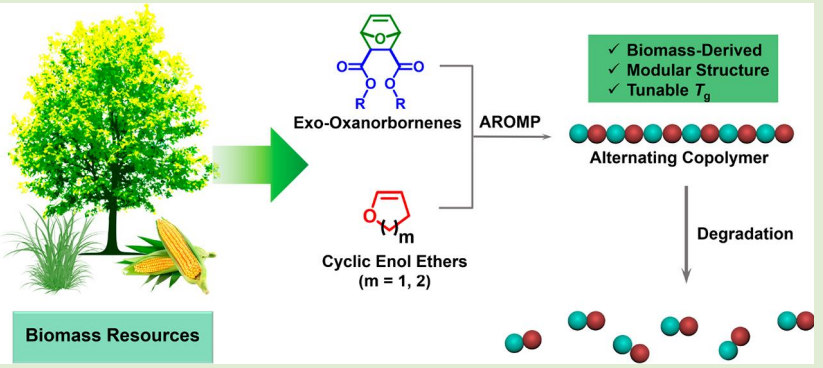

ABSTRACT: Degradable polymers made via ring-opening metathesis polymerization (ROMP) hold tremendous promise as eco-friendly materials. However, most of the ROMP monomers are derived from petroleum resources, which are typically considered less sustainable compared to biomass. Herein, we present a synthetic strategy to degradable polymers by harnessing alternating ROMP of biomass-based cyclic olefin monomers including exo-oxanorbornenes and cyclic enol ethers. A library of well-defined poly(enol ether)s with modular structures, tunable glass transition temperatures, and controlled molecular weights was achieved, demonstrating the versatility of this approach. Most importantly, the resulting copolymers exhibit high degrees of alternation, rendering their backbones fully degradable under acidic conditions.

Synthetic polymer materials are now ubiquitous in modern society, infiltrating every facet of our lives. Nevertheless, less than 10% of polymer waste has been recycled, resulting in pressing environmental and health issues because of their nondegradable all-hydrocarbon backbones.[1,2] Moreover, the vast majority of current commercial polymers are derived from petroleum, which is considered as a finite resource. In the quest of next-generation polymer materials, researchers have recently shifted their attention to the development of sustainable and eco-friendly polymers.[3] As an alternative source to petroleum, biomass is abundant and renewable, making it an ideal resource for the production of polymer materials in the future.[4−6] In addition, it would be highly desirable to incorporate programmable degradability or depolymerizability into the next-generation polymers, facilitating the chemical recycling or biodegradation after their usage lifetime.[7,8]

The rapid advances in ring-opening metathesis polymerization (ROMP) techniques have unlocked the access to a variety of degradable and depolymerizable polymers.[9−13] This can be enabled by the rational design of cyclic alkene monomers that contain degradable functional groups such as acetal,[14−16] ester,[17,18] carbonate,[19] silyl ether,[20] phosphoramidate,[21,22] phosphoester,[23] and enol ether.[24−32] Among those degradable cyclic olefin monomers, 2,3-dihydrofuran (DHF), a biomass-derived and five-membered cyclic enol ether, has recently received significant interest due to its commercial availability and unique ROMP reactivity that allows for its alternating ring-opening metathesis polymerization (AROMP) with a series of comonomers.[25−27,29,31] To date, DHF has been employed in copolymerization with norbornenes,[25] fluorinated norbornenes,[29] diynes,[27] enynes,[26] and very recently endo-oxanorbornenes,[31] to generate a diverse set of acid-degradable poly(enol ether)s.

Oxanorbornene derivatives can be synthesized by Diels−Alder reaction of biomass-derived furan and maleic anhydride.[33,34] In light of this, we reasoned that the ROMP of

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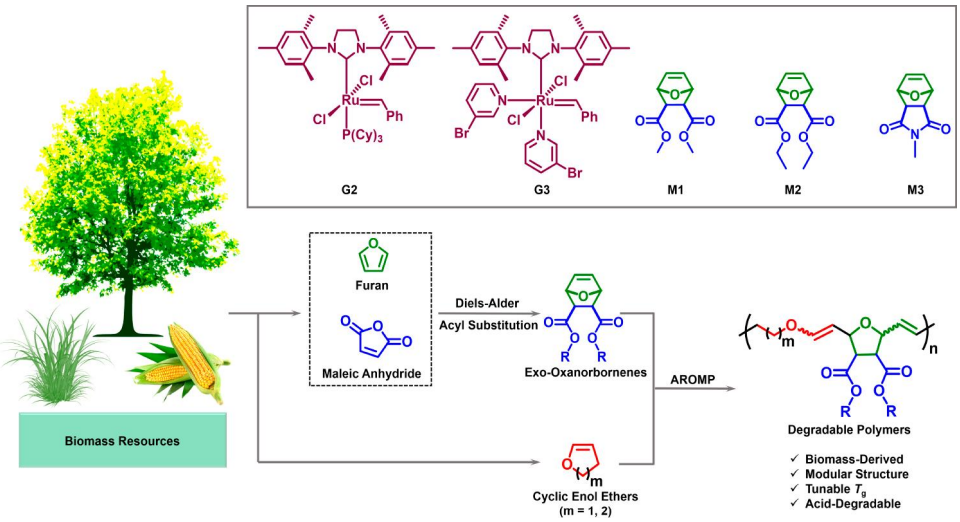

Figure 1. Synthetic strategy to degradable polymers via alternating ring-opening metathesis polymerization of biomass-based exo-oxanorbornenes and cyclic enol ethers. Two cyclic enol ethers, including 2,3-dihydrofuran and 3,4-dihydropyran, were investigated in this study.

oxanorbornene monomers and cyclic enol ethers would give rise to fully biomass-derived degradable polymer materials. Moreover, exo-oxanorbornenes are thermodynamically more stable than their endo analogues, highlighting a longer shelf life by limiting retro-Diels–Alder reaction at ambient temperature.[35,36] In this work, we demonstrate a modular synthetic strategy to biomass-derived degradable polymers by AROMP of exo-oxanorbornene monomers and cyclic enol ethers. Two low-strain cyclic enol ethers including DHF and 3,4-dihydropyran (DHP) were employed for the AROMP with exo-oxanorbornenes, giving rise to a library of well-defined copolymers with high percentages of alternating dyads (Figure 1). Critically, the resulting alternating copolymers were capable of degrading into small molecules under acidic conditions, demonstrating their potential as sustainable and stimuli-responsive materials.

We began our study by the rational design and synthesis of exo-oxanorbornene monomers (Figure 1). Diels–Alder reaction of furan and maleic anhydride led to the formation of exo-7-oxanorbornene-2,3-dicarboxylic anhydride, which was further converted to a series of exo-oxanorbornene monomers (M1–M3) via acyl substitution (Figures 1 and S1–S3). Since oxanorbornene monomers have a slower reactivity than their norbornene analogues in ROMP,[35] we hypothesized that ROMP of oxanorbornene monomers and DHF would generate copolymers with higher degrees of alternation compared to the reported system based on norbornene.[25]

To shed light on the control over the polymerization, ROMP of M1 and DHF was performed in the presence of the Grubbs third catalyst (G3). The molar ratio of DHF to M1 was set to 2:1 in order to suppress the homoaddition of M1. A plot of $\ln([M1]_0/[M1]_t)$ versus time revealed a linear relationship, suggesting pseudo-first-order kinetics consistent with a controlled polymerization (Figure 2a). Furthermore, the molecular weights of copolymers are tunable by adjusting the feed ratios of monomers to Grubbs catalyst, leading to a library of poly(M1-*alt*-DHF) with various degrees of polymerization (DP) and low dispersity (Figure 2b and Table S1, Entries 1–4).

To assess the degrees of alternation, we examined the structure of the copolymers by NMR spectroscopy. According to ^{1}H NMR analysis, the characteristic olefinic proton signals

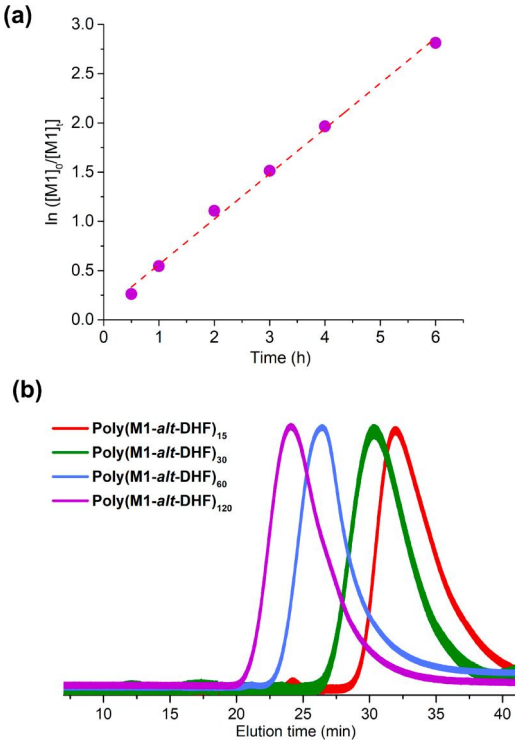

Figure 2. (a) Kinetic study of the AROMP of M1 and DHF targeting a degree of polymerization of 120 for M1. A pseudo-first-order reaction of M1 was observed during the polymerization. (b) GPC traces of alternating copolymers poly(M1-*alt*-DHF) with different degrees of polymerization.

of polyDHF were absent in the ^{1}H NMR spectrum of copolymer poly(M1-*alt*-DHF)$_{120}$, suggesting that no homoaddition of DHF occurred during the polymerization (Figure 3). In addition, the olefinic proton signal of polyM1 was significantly diminished in the copolymer, indicating a suppression of the homoaddition of M1 throughout the AROMP process. ^{13}C NMR data further support the ^{1}H NMR results by showing the absence of alkene carbon signals of polyDHF in the ^{13}C NMR spectrum of the copolymer (Figure 4). Importantly, the integration of proton signals for DHF and

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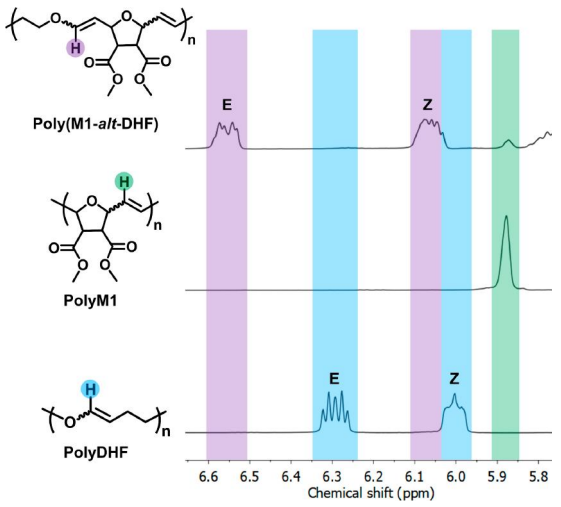

Figure 3. ^{1}H NMR spectra of the alternating copolymer poly(M1-*alt*-DHF)$_{120}$, as well as the two homopolymers including polyM1 and polyDHF in $CDCl_3$ at 25 °C. The olefinic proton signals of polyDHF (highlighted in blue) fully shifted downfield in the spectrum of the alternating copolymer (highlighted in purple), suggesting that no DHF−DHF dyads are present in the copolymer.

M1 repeating units revealed high degrees of alternation (>94% alternating dyads) in all the poly(M1-*alt*-DHF) copolymers, demonstrating an excellent sequence control in the polymer structure (Figures S4−S9 and Table S1, Entries 1−4).

To examine the versatility of this approach, we further employed M2 and M3 for their AROMP with DHF. Surprisingly, the Grubbs third catalyst was not active for the AROMP systems based on M2/DHF and M3/DHF. Nevertheless, the Grubbs second catalyst (G2) successfully promoted the AROMP for M2/DHF and M3/DHF, leading to alternating copolymers: poly(M2-*alt*-DHF) and poly(M3-*alt*-DHF) (Figures S10−S15 and Table S1, Entries 5 and 6). NMR analysis indicates that the degrees of alternation for poly(M2-*alt*-DHF) and poly(M3-*alt*-DHF) are 97% and 99%, respectively (Figures S10 and S14). These results highlight the robustness of the AROMP strategy for generating exo-oxanorbornene/DHF-based alternating copolymers with modular structures and high degrees of alternation.

In comparison to DHF, the ROMP activity of six-membered DHP is significantly lower because of its negligible ring strain. Indeed, no homopolymerization of DHP was observed even under bulk polymerization conditions. Despite the inert nature of DHP in homopolymerization, we hypothesized that copolymerization of exo-oxanorbornene monomers and DHP would kinetically trap DHP repeating units to produce copolymers. To examine our hypothesis, a proof-of-concept study involving ROMP of M1 and DHP was conducted (Figures S16−S18 and Table S1, Entry 7). It is noteworthy to mention that the molar ratio of DHP to M1 was set to 50:1 to enhance the polymerization rate of DHP. Based on NMR analysis, the percentage of M1/DHP dyads in the resulting copolymer is 81%, which is relatively smaller than those copolymers based on the M1/DHF system (Figure S16).

Enol ethers are well-known for their hydrolytic instability under acidic conditions.[24,26] Therefore, we reasoned that the alternating copolymers (i.e., poly(enol ether)s) developed in this study would be acid-degradable. To verify the degradability of poly(M1-*alt*-DHF), an acid-promoted degradation study using hydrochloric acid was designed (Figure 5a). Based on GPC analysis, the molecular weights of poly(M1-*alt*-DHF) gradually decreased as a function of time upon acid treatment

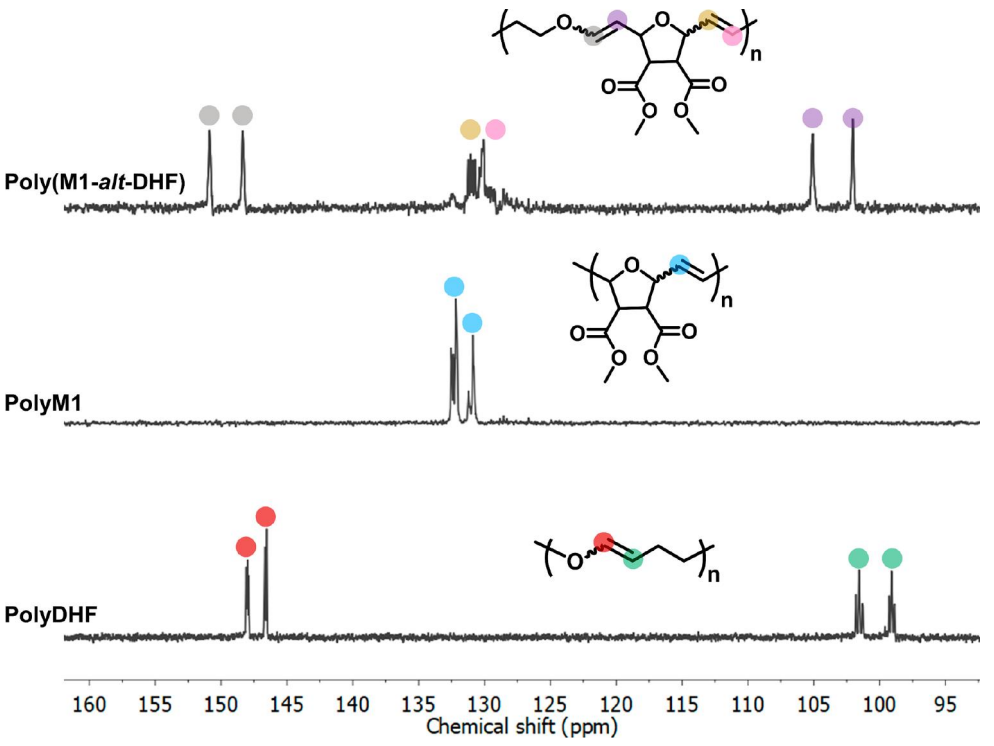

Figure 4. ^{13}C NMR spectra of the alternating copolymer poly(M1-*alt*-DHF)$_{120}$, as well as the two homopolymers including polyM1 and polyDHF in $CDCl_3$ at 25 °C. The ^{13}C signals of alkene in polyDHF (highlighted in red and green) fully shifted downfield in the spectrum of alternating copolymers (highlighted in gray and purple), suggesting that DHF did not undergo homoaddition during the copolymerization process.

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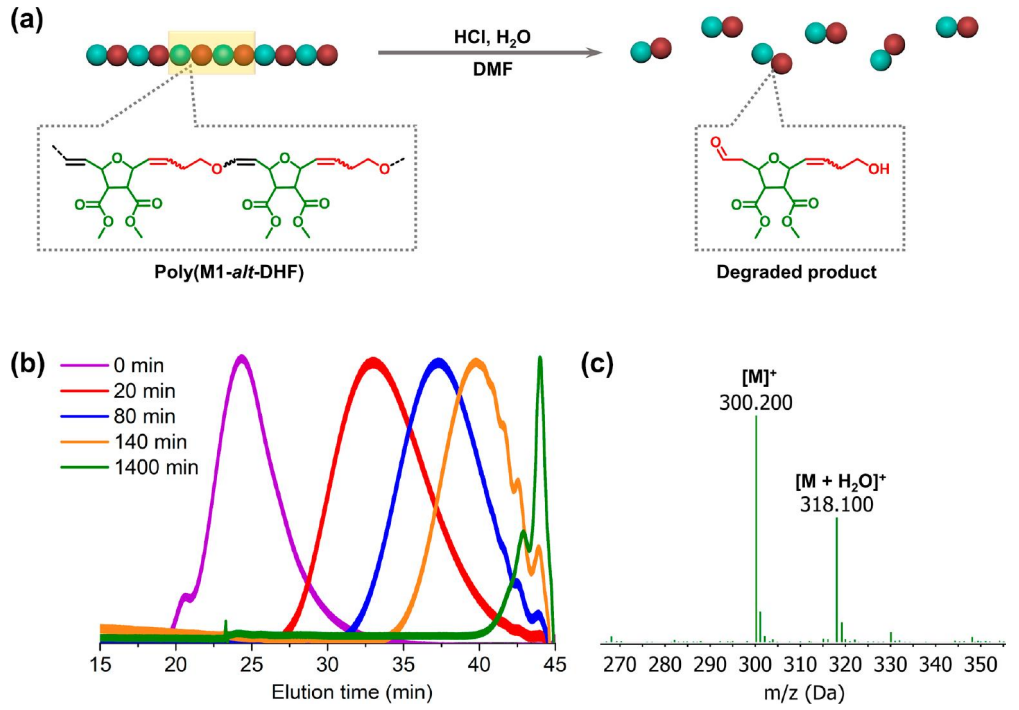

Figure 5. Acid-promoted degradation of poly(M1-*alt*-DHF) in DMF. (A) Schematic illustration of acid-triggered hydrolysis of poly(M1-*alt*-DHF) in the organic phase and (B) GPC traces of poly(M1-*alt*-DHF)$_{120}$ as a function of degradation time. The concentrations of HCl and H_2O are 20 mM and 1.1 M, respectively. (C) Mass spectrum of the final degradation product. The m/z ratio of the molecular ion signal (300.200 Da) is in good agreement with the theoretical molecular weight of the degradation product (300.310 Da).

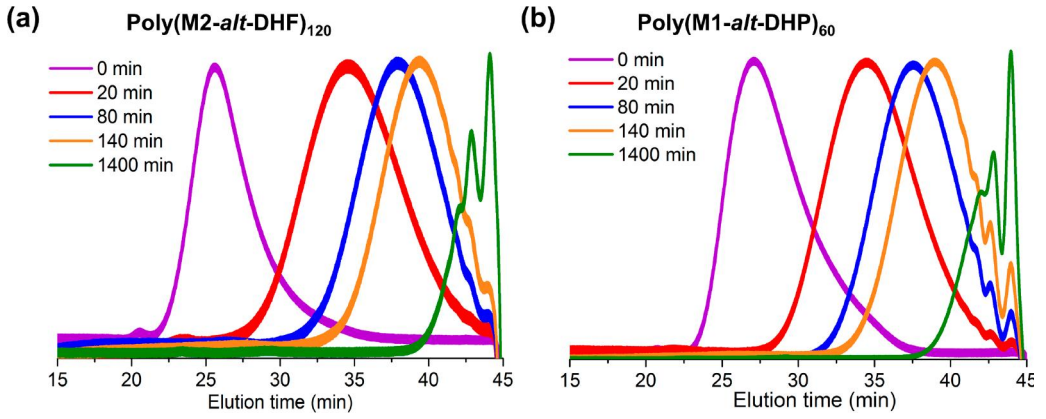

Figure 6. (A) GPC traces of poly(M2-*alt*-DHF)$_{120}$ as a function of degradation time. (B) GPC traces of poly(M1-*alt*-DHP)$_{60}$ as a function of degradation time. The concentrations of HCl and H_2O in DMF are 0.02 and 1.1 M, respectively.

(Figure 5b). Only small fragments below 1000 Da were detectable by GPC after 1400 min of degradation. Mass spectrometry was further used to decipher the structure of the degradation products (Figure 5c and Figure S19). As shown in Figure S19, the molecular ion signal (m/z = 300.20) for the expected hydrolysis product and an ion signal (m/z = 318.10) for the hydrate product were predominant, indicating a significant extent of degradation. This result demonstrates that a high degree of alternation plays a critical role in full degradation of alternating copolymers. To unequivocally attribute the polymer degradation to the hydrolysis of enol ether moieties, a control study on acid-triggered degradation of polyM1 homopolymer was performed. Based on GPC analysis, the molecular weight of polyM1 remained unchanged during the acid treatment, illustrating the acid stability of the poly(exo-oxaborbornene) backbone (Figure S20).

The degradability of all other poly(enol ether)s, including poly(M2-*alt*-DHF), poly(M3-*alt*-DHF), and poly(M1-*alt*-DHP), was further evaluated (Figure 6 and Figure S21). In all cases, the final degradation products were characterized with low molecular weights (<1000 Da) as determined by GPC, suggesting high degrees of degradation under the investigated acidic conditions.

To gain insight into the solvent effect on polymer degradation, we further investigated the heterogeneous degradation behavior of poly(M1-*alt*-DHF) in a 1 M HCl aqueous solution (Figure S22). Compared with homogeneous degradation conducted in DMF (*vide supra*), the degradation of poly(M1-*alt*-DHF) was markedly slower in acidic aqueous solution, showing an appreciable amount of polymer residues after 90 days.

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Finally, the glass transition temperatures (T_g) of the alternating copolymers were determined by differential scanning calorimetry (Figure S23). The highly modular structure of alternating copolymers gave rise to a wide range of glass transition temperatures (11−98 °C), suggesting their potential applications as elastomers and plastics. Notably, poly(M3-*alt*-DHF) bearing the rigid imide structure exhibited the highest T_g (97.7 °C) among all of the copolymers.

In summary, we have presented a robust synthetic approach to biomass-derived degradable polymers by AROMP of exo-oxanorbornenes and cyclic enol ethers. A series of well-defined poly(enol ether)s with modular structure, predetermined molecular weights, low dispersity, and high degrees of alternation were achieved, demonstrating the excellent control over the polymerization and monomer sequence. Because of the high degrees of alternation, the alternating copolymers are capable of fully degrading into small fragments under acidic conditions. Given the widespread applications of degradable polymers in modern biomedicine, nanoimprint lithography, and environmental protection, we envision that the biomass-derived alternating copolymers developed in this study hold great potential as a new class of sustainable and stimuli-responsive materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.3c00608.

Experimental methods and synthetic procedures; ^{1}H and ^{13}C NMR spectra of materials; GPC traces of the polymers; mass spectrum of the degradation products; DSC thermograms of copolymers (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Hao Sun** conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, supervision, writing-original draft, writing-review & editing; **Tarek Ibrahim** data curation; **Angelo Ritacco** data curation, writing-review & editing; **Katie Durkee** data curation, writing-review & editing.

Notes

The authors declare no competing financial interest.

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