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Communication

Ultra-High-Molecular-Weight Poly(Dioxolane): Enhancing the Mechanical Performance of a Chemically Recyclable Polymer

H. Grace Hester, Brooks A. Abel, and Geoffrey W. Coates*

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ABSTRACT: We report a method to synthesize ultra-high-molecular-weight poly(1,3-dioxolane) (UHMW pDXL), a chemically recyclable thermoplastic material with excellent physical properties. We aimed to enhance the mechanical properties of sustainable polymers by increasing the molecular weight and found that UHMW pDXL exhibits similar tensile properties to ultra-high-molecular-weight polyethylene (UHMWPE). The new polymerization method uses metal-free and economically friendly initiators to achieve UHMW pDXL with molecular weights greater than 1000 kDa. The development of UHMW pDXL provides a potential solution for capturing value from plastic waste and addressing the detrimental effects of plastic waste.

In 1985, the term pleistomer (*pleistos* = very many, *mer* = part) was coined to describe very long macromolecular chains composed of more than 15−20 thousand repeat units.[1] Today, these are commonly referred to as ultra-high-molecular-weight (UHMW) polymers. The distinct changes in physical properties of a molecule that occur with increasing molecular weight are classified by the transition from monomer (one part) to oligomer (few parts), to polymer (many parts), and finally to pleistomer (very many parts).[2,3] Progression through these molecular weight domains is accompanied by new and often more robust material properties. Pleistomers exhibit enhanced polymer entanglement compared to analogous polymers of "standard" molecular weight. This allows the polymer chains to be stretched further and absorb more energy before breaking.[1] As a result, UHMW materials are used when the properties of lower-molecular-weight materials are insufficient. A well-known example is ultra-high-molecular-weight polyethylene (UHMWPE). Over 8 times stronger than steel by weight, UHMWPE possesses outstanding wear resistance and the highest impact toughness of any known thermoplastic.[4] Accordingly, UHMWPE has become a dominant material in industrial, medical, and fiber applications.[5]

We hypothesized that the mechanical properties of sustainable polymers, which often suffer from poor material performance, could be enhanced solely by increasing the molar mass to ultrahigh values (>1000 kDa). Sustainable polymers are a promising solution in addressing the increasingly urgent and detrimental effects that plastic waste has on the environment.[6] However, developing a sustainable material with physical property and cost advantages over well-established commodity plastics remains a monumental challenge.[7] Recently, we demonstrated the chemical depolymerization of poly(1,3-dioxolane) (pDXL) directly to its starting material, dioxolane (DXL), in the presence of mixed plastic waste (Figure 1).[8,9] Chemical recycling to monomer (CRM) is a unique recycling strategy where a polymer feedstock is depolymerized to monomer which can then be repolymerized into pristine polymer—creating an opportunity to sustainably capture value

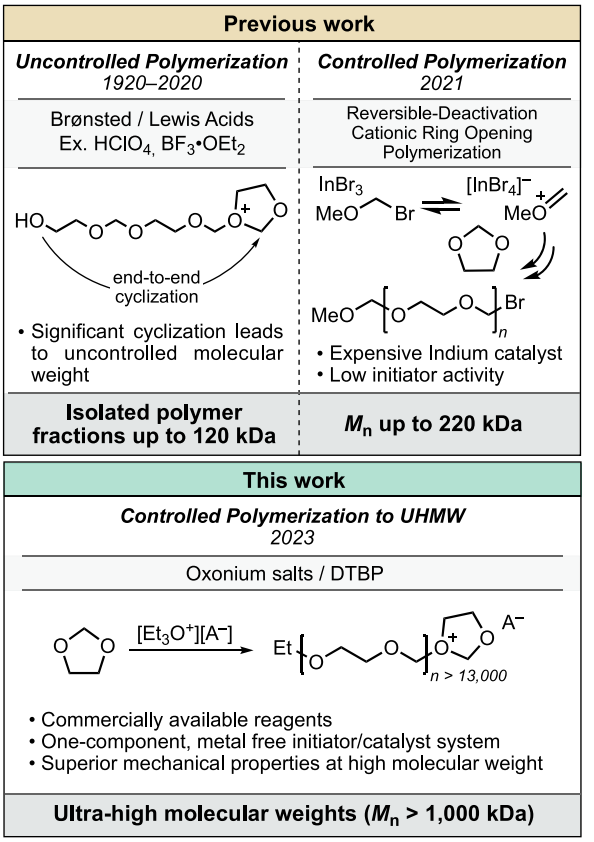

Figure 1. Development of an accessible, controlled DXL polymerization system.

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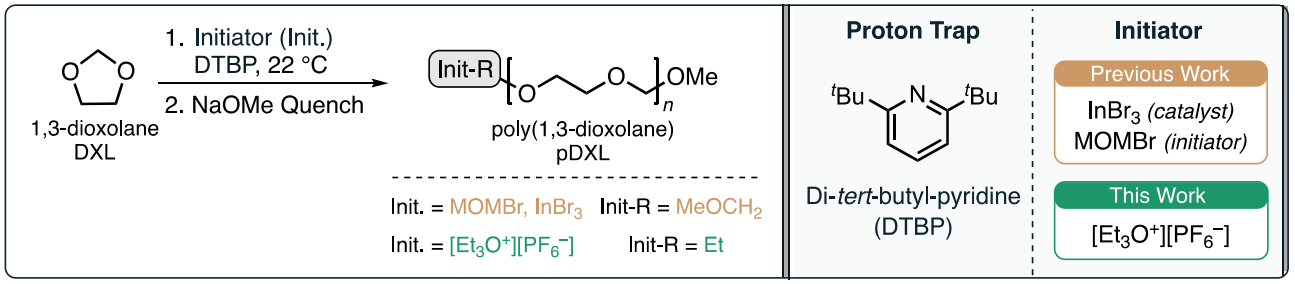
Table 1. Access to UHMW pDXL with Meerwein Salt Initiator in the Presence of DTBP



entry	initiator	$[DXL]_0/[initiator]_0$[a]	$[DTBP]_0/[initiator]_0$[a]	time (h)	conversion[b] (%)	M_n^{theo}[b] (kDa)	M_n^{GPC}[c] (kDa)	$Đ$[c] (M_w/M_n)
1	$InBr_3$/MOMBr	1000	5.0	0.5	85	63	101	1.6
2	$InBr_3$/MOMBr	2000	5.0	1.0	51	76	220	1.6
3	$InBr_3$/MOMBr	4000	5.0	24.0	<1	n.d.[d]	n.d.	n.d.
4	$[Et_3O^+][PF_6^-]$	2000	0.0	0.5	85	126	10	3.0
5	$[Et_3O^+][PF_6^-]$	5000	0.0	1.0	85	314	35	2.7
6	$[Et_3O^+][PF_6^-]$	10000	0.0	4.0	60	444	99	2.3
7	$[Et_3O^+][PF_6^-]$	20000	0.0	4.0	57	844	287	2.0
8	$[Et_3O^+][PF_6^-]$	30000	0.0	24.0	51	1133	327	2.0
9	$[Et_3O^+][PF_6^-]$	2000	5.0	0.5	85	126	129	1.7
10	$[Et_3O^+][PF_6^-]$	4000	5.0	1.0	86	255	240	1.5
11	$[Et_3O^+][PF_6^-]$	5000	5.0	1.0	88	325	228	1.6
12	$[Et_3O^+][PF_6^-]$	10000	5.0	4.0	81	600	717	1.4
13	$[Et_3O^+][PF_6^-]$	20000	5.0	4.0	78	1156	1320	1.9
14	$[Et_3O^+][PF_6^-]$	30000	5.0	16.0	74	1645	1656	2.0
15	$[Et_3O^+][PF_6^-]$	40000	5.0	16.0	75	2222	2031	2.1

[a]$[DXL]_0$ = 8.0 M in DCM. Polymerizations performed in a nitrogen atmosphere at a 4 mmol DXL scale. $InBr_3$ stock solutions prepared in diethyl ether. MOMBr, oxonium salt, and DTBP stock solutions prepared in DCM. DXL, DCM, and DTBP combined before addition of initiator solution. Once viscous, reactions were quenched with 25 μL of 0.5 M NaOMe solution in toluene. [b]Polymerizations were diluted with $CDCl_3$ after quenching until a viscosity appropriate for NMR was achieved. Conversion calculated from integration of monomer vs polymer peaks during ^1H NMR analysis. [c]Determined by GPC in THF, calibrated with polystyrene standards. [d]n.d.: not determined.

from plastic waste.[9] The retention of value from source materials through CRM is advantageous compared to traditional mechanical recycling where reprocessing is complicated by pollutants and additives, resulting in an increasingly frail material.[10] Herein, we report a synthetic method that provides access to UHMW pDXL, which exhibits excellent physical properties comparable to UHMWPE.

Poly(1,3-dioxolane) is synthesized by cationic ring opening polymerization of 1,3-dioxolane, which is commonly employed as a green solvent produced from common industrial C1 and C2 feedstocks.[11] In 2021, our group reported a new route to poly(acetals) using a reversible-deactivation cationic ring opening polymerization (RD-CROP) system capable of producing pDXL of up to 220 kDa (Table 1, entries 1−3).[8] At 180 kDa, pDXL achieved a stress at break (σ_B) of 40 MPa and a strain at break (ε_B) of 720%. Prior to the development of the RD-CROP system, the mechanical characteristics of pDXL were not thoroughly studied, likely due to difficulties in achieving consistent molecular weights.[12] Appreciating the potential of pDXL as a sustainable thermoplastic alternative, we sought to develop a metal-free, economically friendly polymerization system capable of delivering UHMW pDXL.

Synthesis of UHMW materials demands initiators that operate at very low loadings. Triethyl oxonium salts, also known as Meerwein salts, are composed of an oxonium cation and a noncoordinating counterion such as BF_4^-, PF_6^-, and SbF_6^-. Several compositions are commercially available in high-purity crystalline form and are well-known initiators in cationic polymerizations.[13,14] We found that Meerwein salts are effective initiators of DXL polymerization and produce molecular weights up to 98.7 kDa (Table 1, entries 4−8). However, the molecular weights of the resulting polymers could not be predicted by the amount of initiator added to the polymerization and did not increase linearly with monomer conversion (Figure 2b,c). This unpredictability in molecular weights is likely due to adventitious acidic species causing unwanted initiation and chain transfer events. 2,6-Di-*tert*-butylpyridine (DTBP), a non-nucleophilic, strong base is commonly employed as a proton trap in cationic polymerizations of vinylic monomers to prevent initiation of new polymer chains from protic impurities (Figure 2a).[15] Therefore, we hypothesized that the addition of DTBP as a proton trap to the DXL polymerization with a Meerwein salt initiator would allow us to access UHMW pDXL.

The addition of 1−20 equiv of DTBP, relative to initiator, to the polymerization system eliminated the observed unpredictable molecular weight distributions and high dispersities (Table 1, entries 9−15, Figure S2). As expected, control experiments in the presence of DTBP without initiator resulted in no monomer conversion to polymer. Unable to stabilize carbocations or complex with Lewis acids, the sole role of DTBP is to scavenge protic impurities in the polymerization system.[15] By the addition of DTBP, we can avoid several mechanisms by which protic species likely preclude the formation of UHMW's: (1) initiation of new polymer chains; (2) protonation of an existing chain, which catalyzes macrocyclization or transacetalization; or (3) reaction with polymerization counteranion, thereby degrading the counteranion, quenching the active chain end, or releasing new acidic species.[12,16−19] To ensure the elimination of all protic

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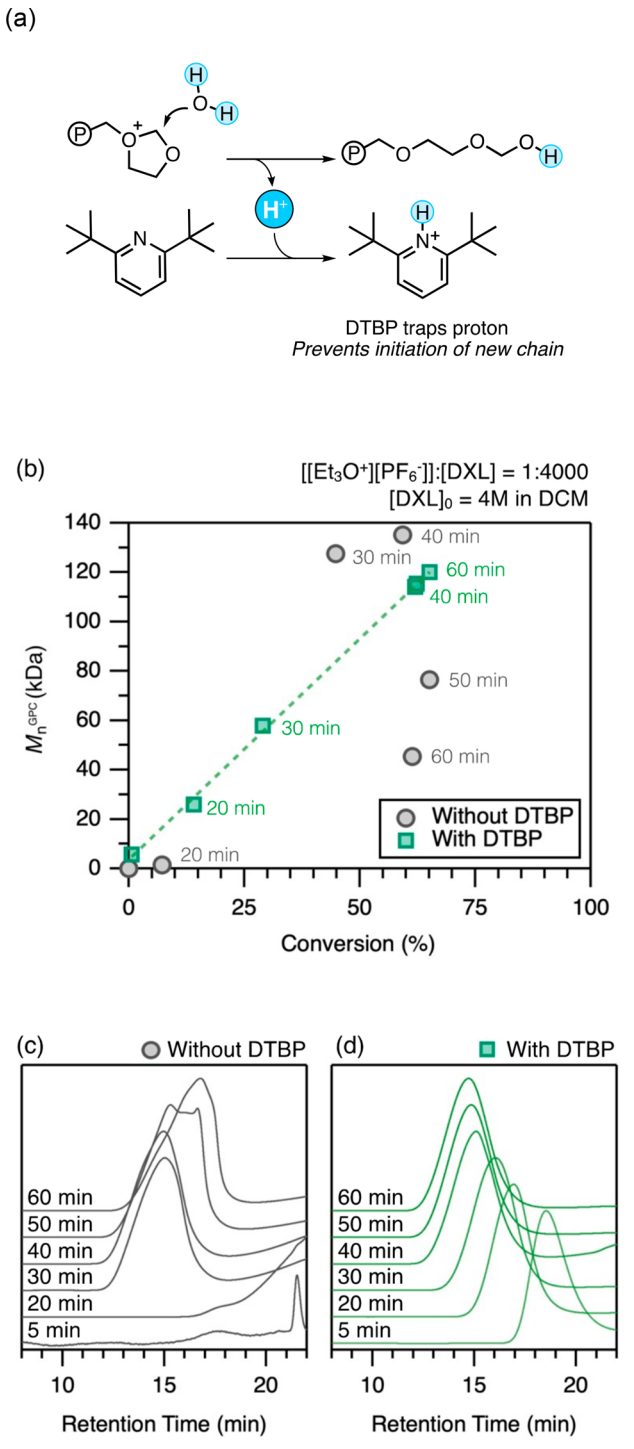
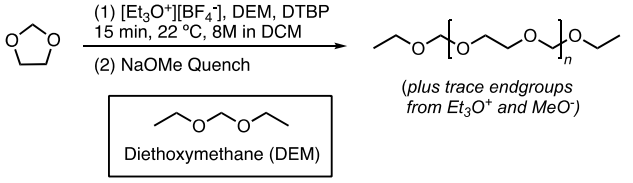


Figure 2. Contrasting polymerization of DXL in the presence or absence of a proton trap with $[[Et_3O^+][PF_6^-]]_0/[DTBP]_0$ = 1:5 (green) or 1:0 (gray). (a) Proposed mechanism of DTBP scavenging protic impurities introduced by trace water reacting with propagating chain end. (b) Molecular weight vs conversion to polymer of DXL polymerization at 5, 20, 30, 40, 50, and 60 min. (c) GPC traces corresponding to the polymerizations without the proton trap shown in panel b. (d) GPC traces corresponding to polymerizations with the proton trap shown in panel b.

impurities and maintain molecular weight control, 5 equiv of DTBP relative to initiator was used in subsequent polymerizations.[8]

Table 2. Use of Diethoxymethane as a Chain-Transfer Agent



$[DEM]_0/[initiator]_0$	M_n^{theo}[a] (kDa)	M_n^{GPC}[b] (kDa)	$Đ$[b] (M_w/M_n)
10	222	219	1.6
20	111	144	1.7
40	56	69	1.7
60	37	49	1.7
100	22	29	1.7

[a]Conversion calculated from integration of monomer vs polymer peaks during ^{1}H NMR analysis. [b]Determined by GPC in THF, calibrated with polystyrene standards.

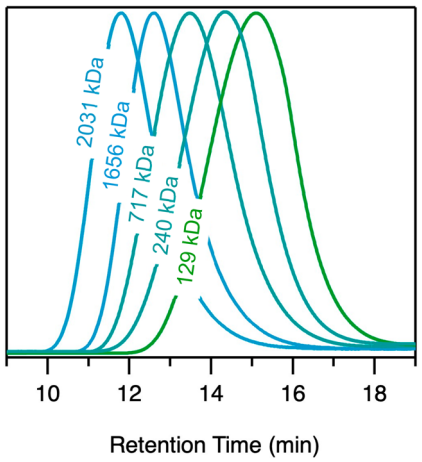


Figure 3. GPC chromatograms of pDXL (Table 1, entries 9, 10, 12, 14, and 15).

We next evaluated the influence of the anionic species on polymerization with three commercially available triethyloxonium Meerwein salts. Interestingly, we found no observable effect of anion identity on polymerization behavior. The lack of a marked difference among BF_4^-, PF_6^-, and $SbCl_6^-$ suggests no consequential coordination between anion and the cationic chain end (Figures S8–S10). This observation is inconsistent with initial evaluations of Meerwein salts as initiators, in which counterion identity influenced polymerization activity in the absence of DTBP.[18−20] A possible explanation of the difference is the susceptibility of the counteranion to protic impurities, which are removed by DTBP in our system.[15,19] For practical reasons, $[Et_3O^+][PF_6^-]$ was selected as the preferred oxonium salt due to the degradation of $[Et_3O^+][BF_4^-]$ at 25 °C, evidenced by transformation from a white crystalline solid to a brown slurry, and the reduced solubility of $[Et_3O^+][SbCl_6^-]$ in DCM. Polymerization using $[Et_3O^+][PF_6^-]$ in DCM demonstrated a linear increase of molecular weight with monomer conversion, indicating controlled polymerization behavior in the presence of 5 equiv of DTBP (Table 1, entries 9−15, Figure 2b,d). Using this system, molecular weights in the ultra-high-molecular-weight regime were achieved, up to 2000 kDa (Table 1, entry 15; Figure 3).

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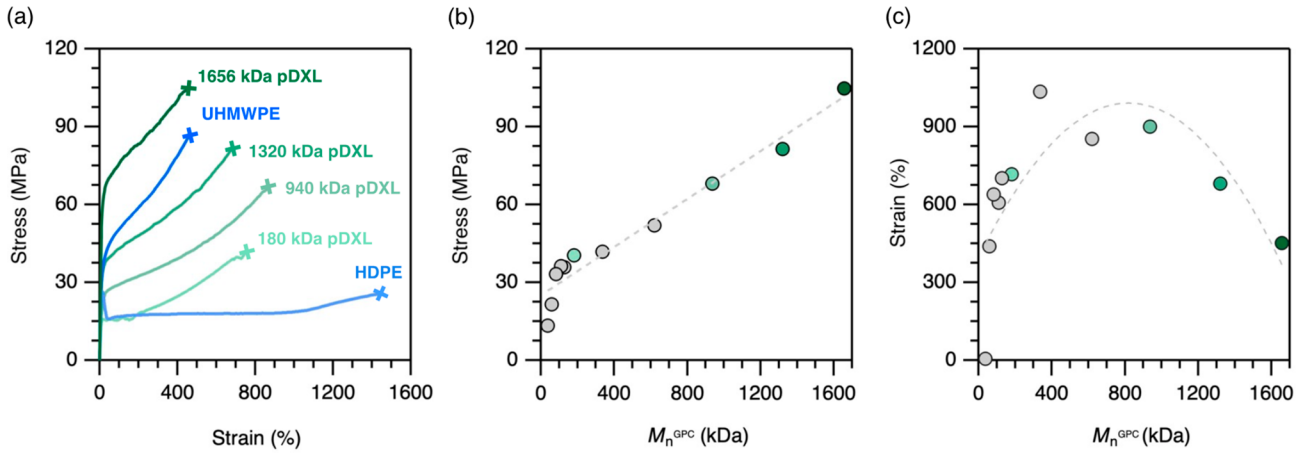

Figure 4. Uniaxial tensile testing results (a) Representative tensile stress−strain strain at break of pDXL over a molecular weight range compared to HDPE and UHMWPE. All samples displayed were prepared by melt processing on a Carver press prior to tensile testing. Fracture points are denoted with ×. Only select samples are shown here for clarity. (b) Representative stress at break vs molecular weight of pDXL. (c) Representative strain at break vs molecular weight of pDXL. Average values and standard deviations for stress, strain, toughness, and Young's modulus are available in the Supporting Information.

Owing to transacetalization, a known phenomenon in ring opening polymerization of cyclic acetals, we consistently observed $Đ$ values ranging from 1.6 to 2.2 regardless of temperature or initial monomer concentration.[12,21] Transacetalization, or chain transfer to a polymer, can be advantageous during the synthesis of UHMW polymers as it allows a "dead" polymer chain to be quickly revived following a transacetalization event. Transacetalization can be leveraged to predictably target lower polymer molecular weights while maintaining extremely low catalyst loading by employing diethoxymethane, an acyclic acetal, as a chain transfer agent (Table 2).

Samples of pDXL ranging from 30 to 1700 kDa were melt processed into dog bone samples and subjected to uniaxial tensile testing (see the Supporting Information).[22,23] Representative stress−strain data demonstrate that pDXL is a ductile and tough thermoplastic with physical properties that vary with molecular weight (Figure 4a). A direct relationship between molecular weight and stress at break was observed for pDXL samples (Figure 4b). Stress at break for a 1656 kDa sample can reach 105 MPa, more than 3× the amount of stress that the analogous 82 kDa sample can withstand before failure. Surprisingly, nonmonotonic strain at break was observed with increasing molecular weight with a maximum ε_B of 1035% at 336 kDa (Figure 4c). After this peak, the strain at break decreased with increasing molecular weights. This phenomenon, which is also observed in polyethylene, is attributed to the rise in tie-segments. Tie-segments refer to lengthy polymer chains that cross the amorphous regions as well as numerous crystalline domains.[24,25] A UHMWPE (∼5000 kg/mol) sample (Figure 4a) subjected to identical testing conditions endured a lower ultimate stress than 1656 kDa pDXL and lower ultimate strain than 1320 kDa pDXL. The mechanical performance of UHMW pDXL achieved here demonstrates the potential for pDXL as a chemically recyclable alternative to current thermoplastics (Figure 4a).

To confirm that chemical recyclability was maintained in the UHMW regime, a 5.00 g sample of 1656 kDa pDXL was depolymerized to DXL in the presence of nonvolatile polymer supported acid catalyst (Dowex-50, 5 wt %). Using a simple distillation apparatus at 150 °C under ambient atmosphere, the collected distillate contained DXL as the only organic product. The fraction contained 4.65 g of DXL, achieving 93% recovery of monomer from UHMW polymer.

In conclusion, we reported a method capable of delivering a sustainable material with excellent mechanical properties. This commercially relevant synthesis of pDXL utilizes inexpensive, nonmetal initiators and a proton trap to access polymer molecular weights an order of magnitude higher than previously reported. The superior performance of UHMW pDXL is illustrated by the ability for a 1656 kDa sample to withstand more than 3 times the amount of stress than an 82 kDa sample before failure. When benchmarked against UHMWPE, UHMW pDXL outperformed in ultimate stress and performed comparably in elongation at break. Moreover, this polymerization system allows for efficient synthesis of polymers with control over the molecular weight, thus making chemically recyclable pDXL accessible and free from the need of toxic or expensive components. In future work, we will continue the development of methods for the controlled polymerization of acetals to aid in the development of chemically recyclable polymers for a circular polymer economy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c01901.

General information, materials, experimental details, supplementary polymerization condition screens, GPC chromatograms, discussion on prepared tensile samples, tensile test data, and additional supporting data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Geoffrey W. Coates − *Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301, United States;* orcid.org/0000-0002-3400-2552; Email: coates@cornell.edu

Authors

H. Grace Hester − *Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New*

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York 14853-1301, United States; orcid.org/0000-0003-3464-4026

Brooks A. Abel − *Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301, United States;* Present Address: B.A.A.: Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States; orcid.org/0000-0002-2288-1975

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.3c01901

Notes

The authors declare no competing financial interest.

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