Macromolecules

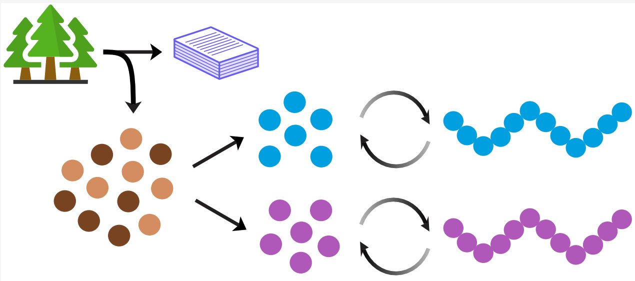
pubs.acs.org/Macromolecules
Article

Unlocking Circularity Through the Chemical Recycling and Upcycling of Lignin-Derivable Polymethacrylates

Ty Christoff-Tempesta, Robert M. O'Dea, and Thomas H. Epps, III*

Cite This: Macromolecules 2023, 56, 9796−9803
Read Online

ABSTRACT: The synthesis of polymers from lignin-derivable compounds can replace petrochemical building blocks with a renewable feedstock. However, the end-of-life management of bioderivable, nonbiodegradable polymers remains an outstanding challenge. Herein, the chemical recycling and upcycling of two higher-glass-transition temperature (>100 °C), lignin-derivable polymethacrylates, poly(syringyl methacrylate) (PSM) and poly(guaiacyl methacrylate) (PGM), is reported. Neat PSM and PGM were thermally depolymerized to quantitative conversions, producing their constituent monomers at high yields and purity. The deconstruction atmosphere influenced the depolymerization reaction order, and depolymerization was thermodynamically favored in air over N_2. Further, monomer bulkiness and volatility impacted depolymerization activation energies. Notably, bulk depolymerization of PSM and PGM was performed without solvent or catalyst to high polymer conversions (89−90 wt %) and monomer yields (86−90 mol %) without byproduct formation. The resultant monomers were then upcycled to narrow-dispersity polymers and phase-separated block polymers. The findings herein offer a pathway to material circularity for higher-performance, lignin-derivable polymethacrylates.



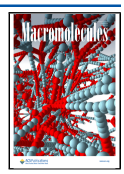
■ INTRODUCTION

The vast majority of polymers manufactured today rely on petrochemical feedstocks for synthetic building blocks.[1,2] These polymers have substantial benefits, but they also engender significant environmental concerns arising from both their start-of-life resource extraction and their end-of-life management and persistence.[3−6] For example, approximately 7% of global oil and gas production is directed towards commodity polymer production and draws on a finite, nonrenewable resource.[7−9] At the same time, few end-of-life pathways are currently capable of repurposing spent polymers into circular pathways or new products with comparable value to the original macromolecules.[2,10−12] Notably, polymers that undergo mechanical recycling—the most prevalent form of polymer recycling today—experience drops in performance arising from events such as chain scission, cross-linking, or the introduction of impurities that result in downcycling to lower-value applications.[13−16]

One route to address start-of-life concerns for commodity polymers is the use of biomass-derived feedstocks, such as lignin, which can be deconstructed into small molecules as potential sustainable building blocks for polymers.[17−20] For instance, lignin is a component of biomass that is separated from cellulose and hemicellulose via industrial pulping operations on the order of 100 Mt annually.[21] Historically, lignin has been considered a waste byproduct due to its complex, recalcitrant chemical structure, and consequently, it is primarily burned for energy.[21,22] Advances in lignin deconstruction to small molecules in recent decades have reinvigorated research on the conversion of lignin—a low-cost, abundant, bioderivable feedstock— into chemicals for commodity products.[23−25] Lignin deconstruction yields a variety of phenolics with either zero, one, or two *ortho*-position methoxy substitutions and a breadth of *para*-position chemical functionalities (e.g., alkyl chains, aldehydes, carboxylic acids).[23,26,27] Lignin-derivable phenolics have in turn been transformed into polymers for applications spanning packaging materials, dental composites, epoxy resins, and microelectronics, among other examples.[23,28−32] Yet, despite the abovementioned start-of-life advantages in monomer sourcing, the responsible end-of-life management of these biobased, nonbiodegradable polymers is unsolved.[33−36]

This manuscript details, for the first time, the chemical recycling and upcycling of two representative lignin-derivable polymethacrylates: poly(syringyl methacrylate) (PSM) and poly(guaiacyl methacrylate) (PGM) (Figure 1). The material

Received: September 27, 2023
Accepted: November 8, 2023
Published: November 22, 2023



https://doi.org/10.1021/acs.macromol.3c01985
Macromolecules 2023, 56, 9796−9803

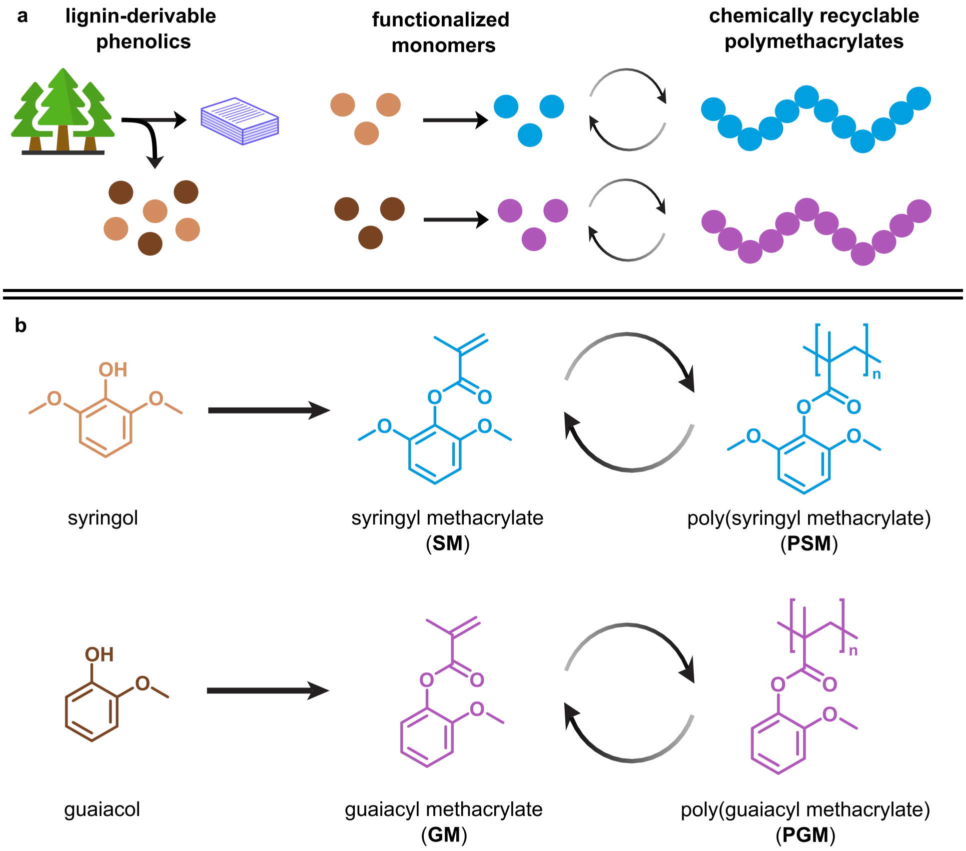


Figure 1. Chemically recyclable and upcyclable high T_g polymethacrylates from lignin-derivable phenolics. (a) In this report, phenolics obtainable from lignin deconstruction were transformed to monomers that could be circularly polymerized and depolymerized. (b) Syringol and guaiacol, two lignin-derivable compounds, were chemically functionalized with methacrylate groups and polymerized by free-radical methods. The resultant polymethacrylates were then thermally depolymerized to monomers that were used in further polymerizations in a circular framework.

properties of PSM and PGM, reported elsewhere, suggest that these polymethacrylates are useful for commercially relevant applications, including thermoformable, boiling-water-stable plastics,[37,38] 3D-printing resins,[31,32,39] and adhesives.[30,40] In these applications, simultaneously sourcing materials from renewable feedstocks and achieving material circularity remains an outstanding challenge.[17,35,37,38] The conditions leading to the quantitative thermal deconstruction of PSM and PGM were investigated, and the volatile products arising from these processes were identified. The kinetics and thermodynamics of deconstruction for each polymer in N_2 and air atmospheres were also examined. Most notably, bulk depolymerizations of PSM and PGM were performed by reactive distillation under dynamic vacuum without added solvent or catalyst to 89−90 wt % conversions and 86−90 mol % monomer yields. The resultant monomers were produced without byproduct formation and were then used to synthesize narrow-dispersity polymers and phase-separated block polymers to demonstrate viable pathways toward the reuse and upcycling of lignin-derivable polymethacrylates. The thermal depolymerization strategy described here unlocks chemical recycling for free-radically synthesized lignin-derivable polymethacrylates to obtain pure constituent monomers at high conversions, enhancing its industrial applicability (and circumventing the need for chemically labile end groups, e.g., from reversible-deactivation radical polymerizations).[41−43] Further, the ability to achieve high depolymerization conversions of bulk PSM and PGM homopolymers under very similar conditions implies that random copolymers of SM and GM (and possibly other lignin-derivable methacrylates)— spanning a ∼100 °C range of T_gs[37]—would efficiently undergo thermal depolymerization in the same reaction environment. Random copolymers could then be synthesized from the resulting constituent monomer mixtures to maintain similar material properties over multiple life cycles, or monomers could be separated (e.g., based on differences in polarity or monomer volatility[31]) to formulate new homopolymers or block polymers, among other potential options.

■ RESULTS AND DISCUSSION

Syringyl methacrylate (SM) and guaiacyl methacrylate (GM) were synthesized from lignin-derivable syringol and guaiacol, respectively, in a single-step esterification reaction with methacryloyl chloride (Figure 1b, see the Supporting Information). PSM and PGM were then prepared via free-radical polymerization to obtain macromolecules with number-average molecular weights (M_n)s of ∼31−43 kg/mol, weight-average molecular weights (M_w)s of ∼107−184 kg/mol, and dispersities ($Đ$)s of 3.4−4.3, as determined by gel permeation chromatography (GPC) calibrated to polystyrene standards (Figure 1b and Table S1). Analysis of polymer thermal transitions by differential scanning calorimetry (DSC) revealed T_gs of 215 and 118 °C for PSM and PGM, respectively, consistent with previous reports (Figure 2a).[37,38]

The deconstruction of PSM and PGM into small-molecule species was first analyzed by thermogravimetric analysis−mass spectrometry (TGA-MS) (Figure 2b−g). This technique simultaneously quantified polymer mass loss caused by

https://doi.org/10.1021/acs.macromol.3c01985
Macromolecules 2023, 56, 9796−9803

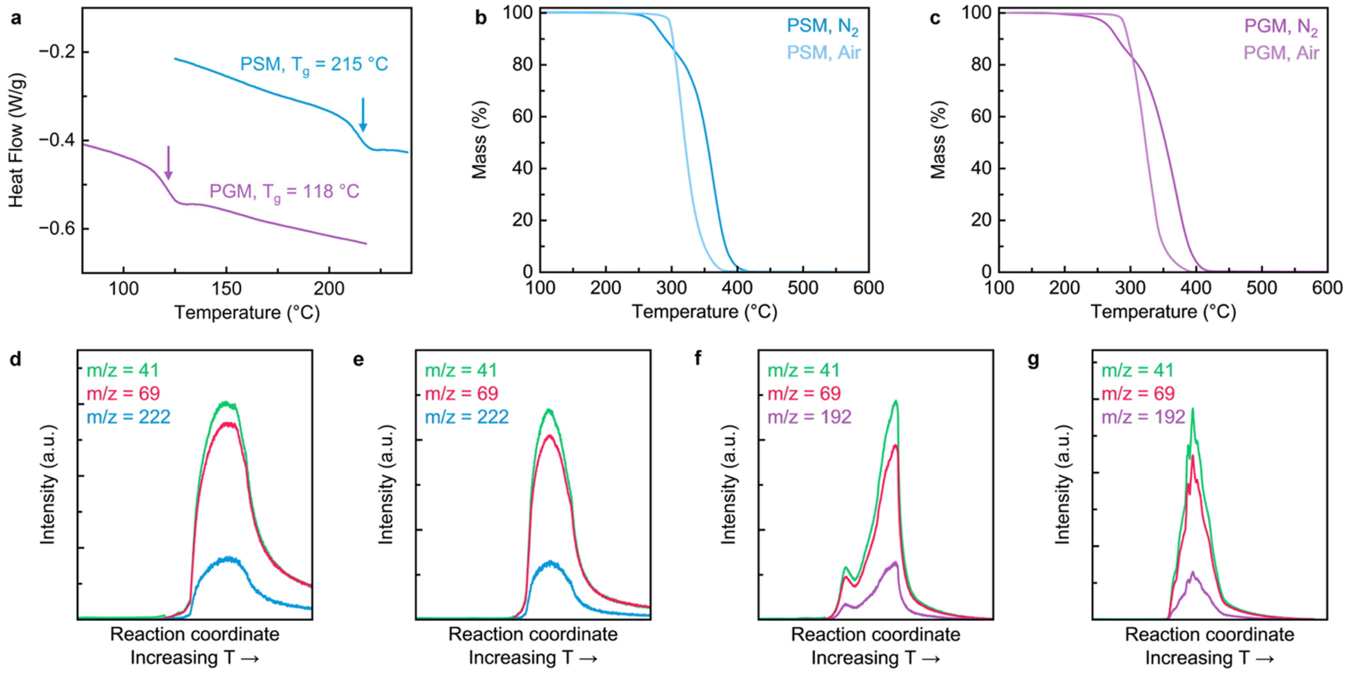


Figure 2. Thermal transitions, thermal deconstruction profiles, and deconstruction products of PSM and PGM. (a) DSC traces on second heating for PSM and PGM with T_gs of 215 and 118 °C, respectively. Traces are shifted vertically for clarity, and T_gs are identified with arrows. TGA curves for (b) PSM and (c) PGM in N_2 (darker curves) and air (lighter curves). (d−g) In-line MS traces obtained during TGA of PSM in (d) N_2 and (e) air, and PGM in (f) N_2 and (g) air (SM expected m/z = 222; GM expected m/z = 192; characteristic methacrylate monomer fragments, expected m/z = 41, 69).[44,45]

thermally induced polymer deconstruction and chemically analyzed the evolved small-molecule products. TGA-MS was performed under both N_2 and air flows to examine the impact of the reaction environment on polymethacrylate deconstruction and extract temperatures corresponding to 5% mass loss ($T_{5\%}$) and 50% mass loss ($T_{50\%}$) for each polymer (Figure 2b,c). For PSM deconstructed in N_2, $T_{5\%}$ = 276 °C and $T_{50\%}$ = 354 °C; for PSM deconstructed in air, $T_{5\%}$ = 298 °C and $T_{50\%}$ = 320 °C; for PGM deconstructed in N_2, $T_{5\%}$ = 266 °C and $T_{50\%}$ = 353 °C; and for PGM deconstructed in air, $T_{5\%}$ = 291 °C and $T_{50\%}$ = 323 °C. TGA data for both PSM and PGM in N_2 implied a two-stage deconstruction process; this pathway has been reported with other polymethacrylates and is hypothesized to result from the unzipping of unsaturated chain ends at lower temperatures followed by random chain scission at higher temperatures.[46−49] In contrast, the unzipping of polymethacrylates at lower temperatures is suppressed in air due to the spontaneous reaction of oxygen with thermally induced polymer radicals to form peroxy radicals that break at higher temperatures.[50] Notably, PSM and PGM quantitatively converted to volatile molecular species across all atmospheres. This result suggested that PSM and PGM thermal depolymerization can be performed with minimal char formation, a useful feature for performing chemical recycling at higher yields with minimal reactor coking.[51,52] Notably, PSM and PGM can be depolymerized without the use of catalysts, which may be prone to poisoning by deconstruction products and in turn have a limited lifespan.[53]

The deconstruction products from the in-line MS profiles corresponding to each TGA trace were also examined (Figure 2d−g). These spectra showed the emergence of species with mass-to-charge (m/z) values of 41 and 69, two known methacrylate ionization fragments,[44,45] and "full" monomer molecular weights (expected m/z of 222 for SM and 192 for GM) over the range of temperatures analyzed. The x-axes of these plots are labeled as a reaction coordinate because of the nonlinear offset between temperatures of polymer mass loss on the TGA profiles and the emergence of molecular species on the mass spectra, attributable to the high normal boiling points of the monomers (b.p.$_{SM}$ ≈ 221 °C, b.p.$_{GM}$ ≈ 131 °C)[31] relative to the maximum temperature (200 °C) of the line connecting the TGA instrument and MS detector (Figure S1). The capability to quantitatively deconstruct cross-linked PGM to its monomers was also confirmed (Figure S2).

The kinetics and thermodynamics of polymer deconstructions were modeled to provide insight into the influence of polymer structure and reaction atmosphere on deconstruction pathways and inform appropriate conditions for bulk chemical recycling efforts.[54,55] Herein, a TGA-based protocol was employed to capture the deconstruction kinetics and activation energies for PSM and PGM in N_2 and air atmospheres. At a given temperature above a polymer's onset of thermal degradation, the change in conversion (α, defined as the fractional mass of polymer deconstructed relative to its initial mass) is related to time (t) by

$$\frac{d\alpha}{dt} = k(1-\alpha) \quad \text{for a first-order reaction} \tag{1}$$

or

$$\frac{d\alpha}{dt} = k(1-\alpha)^2 \quad \text{for a second-order reaction} \tag{2}$$

in which k is a rate constant describing the kinetics of the deconstruction reaction under isothermal conditions.[56−58] These equations integrate to[56−58]

$$-\ln(1-\alpha) = kt \quad \text{for a first-order reaction} \tag{3}$$

or

https://doi.org/10.1021/acs.macromol.3c01985
Macromolecules 2023, 56, 9796−9803

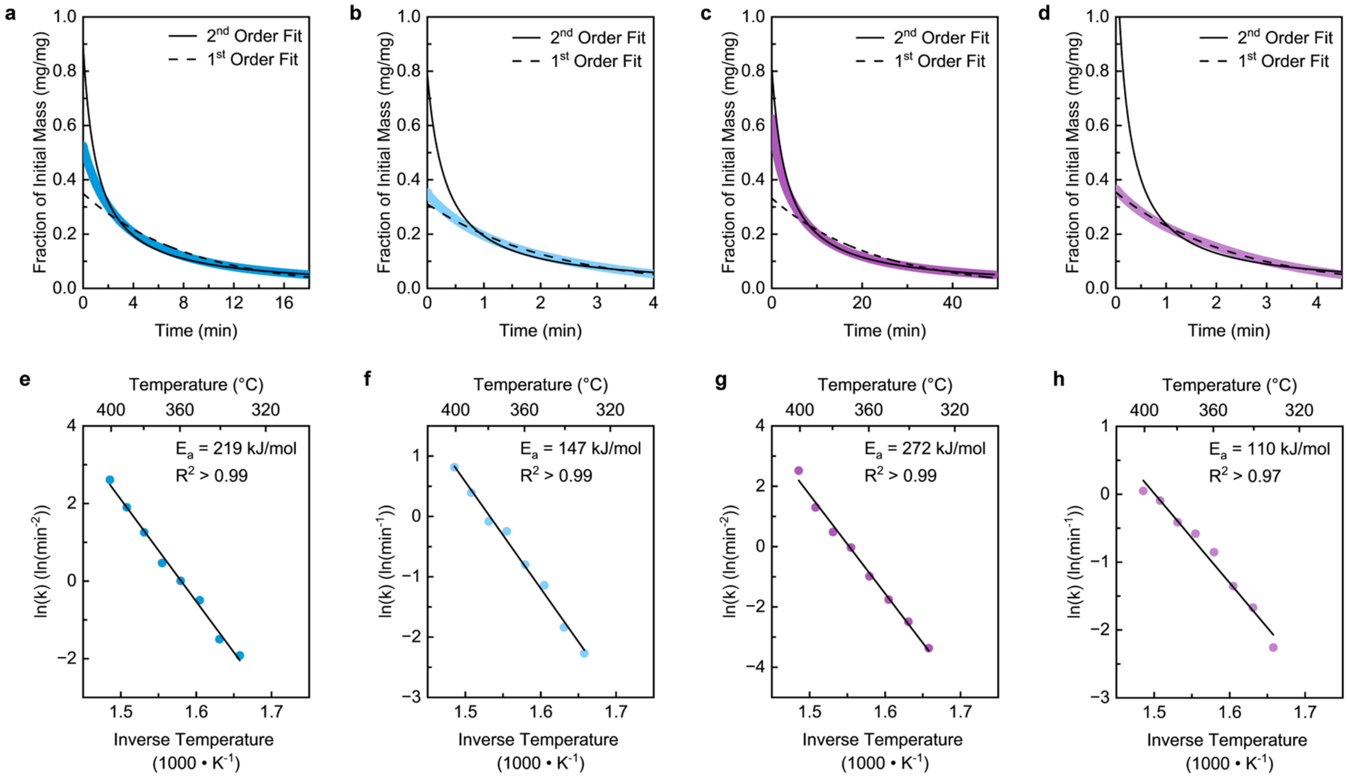


Figure 3. Kinetics and thermodynamics of lignin-derivable polymethacrylate deconstructions. (a–d) Depolymerization kinetic rate constants extracted from the slopes of the best-fit lines for PSM and PGM deconstructions in N_2 and air. Representative first- and second-order fittings for isothermal TGA holds at 350 °C are shown for (a) PSM in N_2, (b) PSM in air, (c) PGM in N_2, and (d) PGM in air. (e–h) Rate constants from isothermal holds over a range of temperatures were linearized to an Arrhenius relationship for (e) PSM in N_2, (f) PSM in air, (g) PGM in N_2, and (h) PGM in air.

$$(1 - \alpha)^{-1} - 1 = kt \quad \text{for a second-order reaction} \tag{4}$$

Rate constants were extracted from the slopes of best-fit lines using eqs 3 and 4 over a range of deconstruction isotherms (Figure 3a–d).[56−58] Notably, the polymethacrylates' depolymerization reaction orders changed based on the chemical environment: PSM and PGM deconstruction kinetics fit a first-order reaction in air and a second-order reaction in N_2. This difference may be attributed to the different reaction mechanisms described previously and demonstrated in Figure 2b,c.[46−50]

Finally, an effective activation energy for deconstruction, E_a, was calculated based on an Arrhenius relationship

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{5}$$

that linearizes to

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \tag{6}$$

in which A is a pre-exponential factor, R is the ideal gas constant, and T is the temperature.[56−58] E_a was thus extracted from plots of ln (k) versus inverse temperature for PSM and PGM in N_2 and air to find E_{a,PSM,N_2} = 219 kJ/mol; $E_{a,PSM,Air}$ = 147 kJ/mol; E_{a,PGM,N_2} = 272 kJ/mol; and $E_{a,PGM,Air}$ = 110 kJ/mol (Figure 3e–h). $E_{a,Air}$ for each polymer was lower than E_{a,N_2}, which suggested a catalytic role of oxygen in the polymethacrylates' deconstruction to small molecules.[50,59] Additionally, E_{a,PGM,N_2} was higher than E_{a,PSM,N_2}, but $E_{a,PGM,Air}$ was lower than $E_{a,PSM,Air}$. These trends implied that the determined E_a may be influenced by both the activation energy for the depolymerization reaction and the energy required to volatilize monomer products. The depolymerization of PSM was likely energetically favored over the depolymerization of PGM due to the relatively higher steric bulkiness of the SM constituents, leading to a lower E_a for PSM than PGM in N_2.[60,61] However, if a catalytic reactant like oxygen lowered E_a sufficiently, then the measured E_a values could be influenced by the energy input needed to volatilize the deconstruction products off of the TGA pan.[59] In this case, the substantially higher boiling point of SM versus GM (b.p.$_{SM}$ ≈ 221 °C, b.p.$_{GM}$ ≈ 131 °C)[31] may have led to a lower measured E_a for PGM than PSM in air. Despite the sensitivity to monomer volatilities, the E_a's determined by the TGA-based method employed here are useful for the practical implementation of chemical recycling processes based on monomer volatilization (e.g., bulk depolymerization with monomer recovery by distillation).

The insights gleaned about the conditions that enable efficient PSM and PGM depolymerization were harnessed to perform bulk thermal deconstructions to high yields (Figure 4). In these experiments, PSM or PGM were heated under dynamic vacuum (4 h, 300 °C), and the resultant small-molecule products were distilled and captured in a liquid nitrogen cold trap. Small-molecule products were characterized by gas chromatography−mass spectrometry (GC-MS) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, and the remnant polymer fractions were characterized by GPC. In particular, for PSM, the 300 °C deconstruction temperature

https://doi.org/10.1021/acs.macromol.3c01985
Macromolecules 2023, 56, 9796−9803

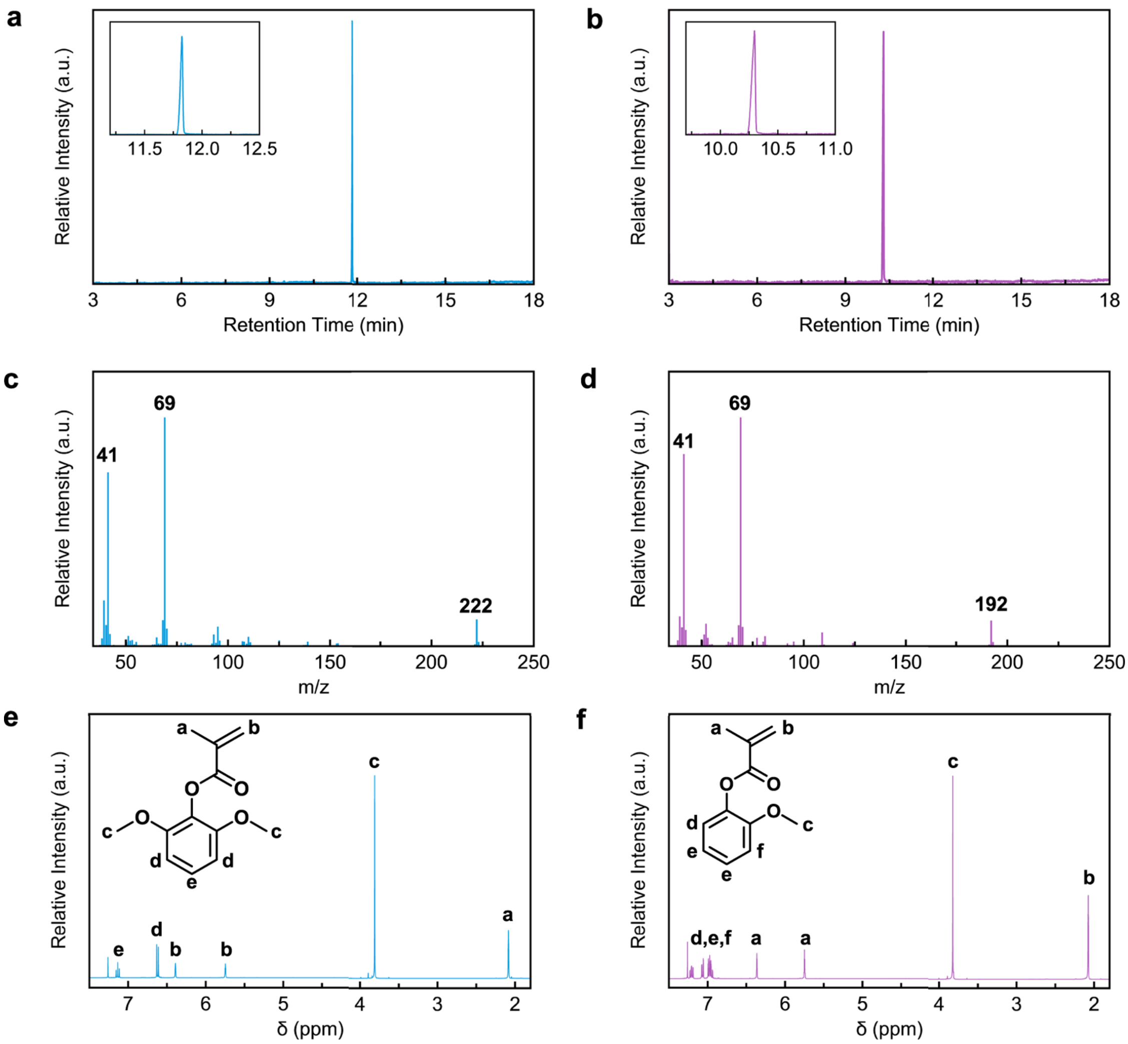


Figure 4. Characterization of PGM and PSM bulk deconstruction products from reactive distillation. (a, b) Gas chromatograms of molecular outputs from bulk deconstruction of (a) PSM and (b) PGM. Insets provide zoomed-in profiles of the GC traces. (c, d) In-line MS data for the major GC peak from (c) PSM deconstruction in panel (a) and (d) PGM deconstruction in panel (b). (e, f) ^{1}H NMR spectrum of (e) PSM deconstruction product and (f) PGM deconstruction product. Assignments of peaks to constituent monomer protons are shown for reference.

provides an ideal processing window (∼100 °C) between the T_g and the upcycling conditions. Further, the 300 °C depolymerization falls below deconstruction temperatures typical of poly(methyl methacrylate) (PMMA) pyrolysis methods (≈350−600 °C).[55]

PSM and PGM were deconstructed in bulk to small-molecule products with 90 and 89 wt % polymer conversions and 90 and 86 mol % small-molecule yields, respectively. These yields are at the higher end of the ∼30−90 wt % monomer yields typical of optimized PMMA thermolysis strategies.[62] The close matches between polymer conversions and collected small-molecule yields suggested that minimal or no gaseous byproducts (e.g., CO_2) evolved under the employed depolymerization conditions. Analysis of remnant polymer molecular weights after deconstruction by GPC showed decreases in both M_n and M_w relative to those of the starting materials (Table S1). Evaluation of the small-molecule products by GC-MS revealed a single GC peak for each acquired product fraction (Figure 4a,b). Mass spectra from these GC peaks corresponded to the constituent methacrylate monomers (Figure 4c,d), as determined by the presence of methacrylate fragments[44,45] and monomer molecular weights that match the above-mentioned TGA-MS results. Additionally, peaks in the ^{1}H NMR spectra of the deconstruction outputs were fully assignable to the corresponding monomers (Figure 4e,f). In contrast, the thermal deconstruction of PMMA is known to yield noxious byproducts (e.g., methyl isobutyrate, methyl pyruvate) that disrupt polymerizations and thus limit monomer recycling.[63] The suppression of byproduct formation in PSM and PGM thermal depolymerization is likely enabled by the use of lower depolymerization temperatures than those typically employed in PMMA pyrolysis and eliminates the need to purify the distillate prior to repolymerization.[55,63] Altogether, the data indicated that PSM and PGM were depolymerized in high yields to pure monomers under these conditions.

Finally, new polymers were synthesized from the outputs of PSM and PGM bulk depolymerizations to demonstrate the potential for circularity and upcycling of lignin-derivable polymethacrylates. First, activators regenerated by electron transfer−atom transfer radical polymerization (ARGET-ATRP) was employed to synthesize PSM and PGM from recovered monomers.[64,65] PSM upcycled by ARGET-ATRP demonstrated a dispersity significantly narrower ($Đ$ = 1.2) than

https://doi.org/10.1021/acs.macromol.3c01985
Macromolecules 2023, 56, 9796−9803

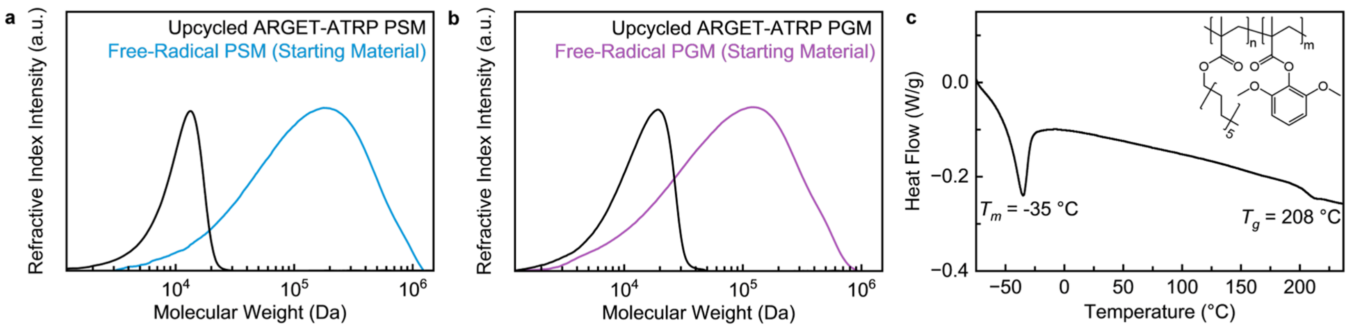


Figure 5. Low dispersity and block polymers synthesized from SM and GM bulk depolymerization products. (a) GPC traces of PSM synthesized by ARGET-ATRP ($Đ$ = 1.2) using monomer from bulk depolymerization and its free-radically synthesized starting material ($Đ$ = 4.3). (b) GPC traces of PGM obtained via ARGET-ATRP of reclaimed monomer ($Đ$ = 1.4) and its free-radically synthesized starting material ($Đ$ = 3.4). (c) DSC trace on the second heating of P(LM-*b*-SM) using SM from bulk depolymerization exhibited a melting peak at −35 °C and a T_g at 208 °C.

that of the starting material synthesized by free-radical polymerization ($Đ$ = 4.3, Figure 5a). Similarly, PGM obtained by ARGET-ATRP of recovered monomer exhibited a substantially lower dispersity ($Đ$ = 1.4) than its free-radical-synthesized starting material ($Đ$ = 3.4, Figure 5b). The generation of a block polymer also was realized from the depolymerization products of PSM. In this case, lauryl methacrylate (LM) was polymerized via ARGET-ATRP and then chain extended with recovered SM to produce a phase-separated block polymer, P(LM-*b*-SM) (Table S1). Lauryl methacrylate was chosen for this synthesis because it is bioderivable from lauric and lauryl acids, components of numerous plant oils,[66,67] thus foreshadowing the potential of an "all-biobased" block polymer. DSC data obtained for P(LM-*b*-SM) revealed a melting peak at −35 °C corresponding to the LM block[68] and a T_g at 208 °C corresponding to the SM block (Figure 5c). These results suggested that P(LM-*b*-SM) may be useful in, e.g., thermoplastic elastomer applications, in which having phase-separated blocks with distinct thermal characteristics is important to material function.[69−71] In total, the outputs of PGM and PSM bulk depolymerization were useful as starting materials for macromolecules of equal or greater value than those of the initial polymers.

■ CONCLUSIONS

Lignin-derivable phenolics offer potential as sustainable alternatives to petrochemically derived aromatic building blocks for polymer production. Notably, facile functionalization and polymerization of these phenolics enables the synthesis of high T_g (>100 °C), glassy polymers. Despite these feedstock and thermal performance advantages, responsible end-of-life management for lignin-derivable polymethacrylates has remained an outstanding challenge. Here, the chemical recycling and upcycling of two lignin-derivable polymethacrylates was demonstrated. PSM and PGM were thermally depolymerized in N_2 and air to quantitative conversions, and the constituent monomers were identified as the primary deconstruction outputs using TGA-MS. Analysis of the depolymerization kinetics captured a sensitivity of the reaction order to the deconstruction atmosphere. Measurements of thermodynamic parameters of depolymerization uncovered a catalytic role of oxygen in polymer deconstruction and a thermodynamic balance between energy inputs required for deconstruction versus monomer volatilization based on reaction pathways. Finally, depolymerization of the lignin-derivable polymethacrylates was extended to the bulk to obtain SM and GM monomers from PSM and PGM, respectively, in high yields (86−90 mol %) and absent byproduct formation. The resultant monomers served as building blocks for narrow-dispersity polymers ($Đ$ = 1.2−1.4) and phase-separated block polymers, demonstrating methods for upcycling lignin-derivable monomers over multiple life cycles. In summary, the results herein present a bulk, catalyst-free strategy to chemically recycle lignin-derivable polymethacrylates with high yields and monomer purity and illustrate the utility of the resulting monomer for upcycling, offering a path towards circular material economies for lignin-derivable polymers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.3c01985.

Materials and methods; compiled GPC results; TGA-MS of SM; TGA-MS of cross-linked PGM (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Thomas H. Epps, III − *Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States; Department of Materials Science and Engineering and Center for Research in Soft matter and Polymers (CRiSP), University of Delaware, Newark, Delaware 19716, United States;* orcid.org/0000-0002-2513-0966; Email: thepps@udel.edu

Authors

Ty Christoff-Tempesta − *Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States;* orcid.org/0000-0002-6551-6599

Robert M. O'Dea − *Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States;* orcid.org/0000-0002-7280-4687

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.3c01985

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

T.C.-T. and T.H.E., III are grateful for the financial support from the Army Research Office under Cooperative Agreement Number W911NF-22-2-0257. R.M.O and T.H.E., III thank the National Science Foundation (NSF) Growing Convergence Research program (NSF GCR CMMI 1934887) in Materials Life Cycle Management for supporting the initial experiments. R.M.O. and T.H.E., III thank the Center for Plastics Innovation, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award DE-SC0021166, for support during the writing of this manuscript. The views and conclusions herein are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Office, the Department of Energy, the National Science Foundation, or the U.S. Government.

■ REFERENCES

(1) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable polymers from renewable resources. *Nature* **2016**, *540* (7633), 354−362.

(2) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **2017**, *3* (7), No. e1700782.

(3) Jehanno, C.; Alty, J. W.; Roosen, M.; De Meester, S.; Dove, A. P.; Chen, E. Y. X.; Leibfarth, F. A.; Sardon, H. Critical advances and future opportunities in upcycling commodity polymers. *Nature* **2022**, *603* (7903), 803−814.

(4) Harrison, R. M.; Hester, R. E. *Plastics and the Environment*. Royal Society of Chemistry: Cambridge, UK, 2019.

(5) Hinton, Z. R.; Talley, M. R.; Kots, P. A.; Le, A. V.; Zhang, T.; Mackay, M. E.; Kunjapur, A. M.; Bai, P.; Vlachos, D. G.; Watson, M. P.; Berg, M. C.; Epps, T. H., III; Korley, L. T. J. Innovations toward the valorization of plastics waste. *Annu. Rev. Mater. Res.* **2022**, *52* (1), 249−280.

(6) Garrison, J. B.; Hughes, R. W.; Sumerlin, B. S. Backbone degradation of polymethacrylates via metal-free ambient-temperature photoinduced single-electron transfer. *ACS Macro Lett.* **2022**, *11* (4), 441−446.

(7) Williams, C. K.; Hillmyer, M. A. Polymers from renewable resources: a perspective for a special issue of polymer reviews. *Polym. Rev.* **2008**, *48* (1), 1−10.

(8) Okada, M. Chemical syntheses of biodegradable polymers. *Prog. Polym. Sci.* **2002**, *27* (1), 87−133.

(9) Weisz, P. B. Basic choices and constraints on long-term energy supplies. *Phys. Today* **2004**, *57* (7), 47−52.

(10) Nguyen, S. T.; McLoughlin, E. A.; Cox, J. H.; Fors, B. P.; Knowles, R. R. Depolymerization of hydroxylated polymers via light-driven C−C bond cleavage. *J. Am. Chem. Soc.* **2021**, *143* (31), 12268−12277.

(11) Rorrer, N. A.; Nicholson, S.; Carpenter, A.; Biddy, M. J.; Grundl, N. J.; Beckham, G. T. Combining reclaimed PET with bio-based monomers enables plastics upcycling. *Joule* **2019**, *3* (4), 1006−1027.

(12) Hodges, M. N.; Elardo, M. J.; Seo, J.; Dohoda, A. F.; Michael, F. E.; Golder, M. R. Upcycling of polybutadiene facilitated by selenium-mediated allylic amination. *Angew. Chem., Int. Ed.* **2023**, *62* (20), No. e202303115.

(13) Schyns, Z. O. G.; Shaver, M. P. Mechanical recycling of packaging plastics: a review. *Macromol. Rapid Commun.* **2021**, *42* (3), No. 2000415.

(14) Assadi, R.; Colin, X.; Verdu, J. Irreversible structural changes during PET recycling by extrusion. *Polymer* **2004**, *45* (13), 4403−4412.

(15) Law, K. L.; Narayan, R. Reducing environmental plastic pollution by designing polymer materials for managed end-of-life. *Nat. Rev. Mater.* **2022**, *7* (2), 104−116.

(16) Gallin, C. F.; Lee, W.-W.; Byers, J. A. A simple, selective, and general catalyst for ring closing depolymerization of polyesters and polycarbonates for chemical recycling. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202303762.

(17) Haque, F. M.; Ishibashi, J. S. A.; Lidston, C. A. L.; Shao, H.; Bates, F. S.; Chang, A. B.; Coates, G. W.; Cramer, C. J.; Dauenhauer, P. J.; Dichtel, W. R.; Ellison, C. J.; Gormong, E. A.; Hamachi, L. S.; Hoye, T. R.; Jin, M.; Kalow, J. A.; Kim, H. J.; Kumar, G.; LaSalle, C. J.; Liffland, S.; Lipinski, B. M.; Pang, Y.; Parveen, R.; Peng, X.; Popowski, Y.; Prebihalo, E. A.; Reddi, Y.; Reineke, T. M.; Sheppard, D. T.; Swartz, J. L.; Tolman, W. B.; Vlaisavljevich, B.; Wissinger, J.; Xu, S.; Hillmyer, M. A. Defining the macromolecules of tomorrow through synergistic sustainable polymer research. *Chem. Rev.* **2022**, *122* (6), 6322−6373.

(18) Leibfarth, F. A.; Moreno, N.; Hawker, A. P.; Shand, J. D. Transforming polylactide into value-added materials. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50* (23), 4814−4822.

(19) Wu, X.; Galkin, M. V.; Stern, T.; Sun, Z.; Barta, K. Fully lignocellulose-based PET analogues for the circular economy. *Nat. Commun.* **2022**, *13* (1), No. 3376.

(20) Trotta, J. T.; Watts, A.; Wong, A. R.; LaPointe, A. M.; Hillmyer, M. A.; Fors, B. P. Renewable thermosets and thermoplastics from itaconic acid. *ACS Sustainable Chem. Eng.* **2019**, *7* (2), 2691−2701.

(21) Bajwa, D. S.; Pourhashem, G.; Ullah, A. H.; Bajwa, S. G. A concise review of current lignin production, applications, products and their environmental impact. *Ind. Crops Prod.* **2019**, *139*, No. 111526.

(22) Behling, R.; Valange, S.; Chatel, G. Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: what results? What limitations? What trends? *Green Chem.* **2016**, *18* (7), 1839−1854.

(23) Bass, G. F.; Epps, T. H., III Recent developments towards performance-enhancing lignin-based polymers. *Polym. Chem.* **2021**, *12* (29), 4130−4158.

(24) Beckham, G. T.; Johnson, C. W.; Karp, E. M.; Salvachúa, D.; Vardon, D. R. Opportunities and challenges in biological lignin valorization. *Curr. Opin. Biotechnol.* **2016**, *42*, 40−53.

(25) Sethupathy, S.; Murillo Morales, G.; Gao, L.; Wang, H.; Yang, B.; Jiang, J.; Sun, J.; Zhu, D. Lignin valorization: status, challenges and opportunities. *Bioresour. Technol.* **2022**, *347*, No. 126696.

(26) Yang, C.; Chen, H.; Peng, T.; Liang, B.; Zhang, Y.; Zhao, W. Lignin valorization toward value-added chemicals and fuels via electrocatalysis: a perspective. *Chin. J. Catal.* **2021**, *42* (11), 1831−1842.

(27) Sun, Z.; Bottari, G.; Afanasenko, A.; Stuart, M. C. A.; Deuss, P. J.; Fridrich, B.; Barta, K. Complete lignocellulose conversion with integrated catalyst recycling yielding valuable aromatics and fuels. *Nat. Catal.* **2018**, *1* (1), 82−92.

(28) Fang, L.; Zhou, J.; Tao, Y.; Wang, Y.; Chen, X.; Chen, X.; Hou, J.; Sun, J.; Fang, Q. Low dielectric fluorinated polynorbornene with good thermostability and transparency derived from a biobased allylphenol (eugenol). *ACS Sustainable Chem. Eng.* **2019**, *7* (4), 4078−4086.

(29) Nicastro, K. H.; Kloxin, C. J.; Epps, T. H., III Potential lignin-derived alternatives to bisphenol A in diamine-hardened epoxy resins. *ACS Sustainable Chem. Eng.* **2018**, *6* (11), 14812−14819.

(30) Wang, S.; Shuai, L.; Saha, B.; Vlachos, D. G.; Epps, T. H., III From tree to tape: direct synthesis of pressure sensitive adhesives from depolymerized raw lignocellulosic biomass. *ACS Cent. Sci.* **2018**, *4* (6), 701−708.

(31) O'Dea, R. M.; Pranda, P. A.; Luo, Y.; Amitrano, A.; Ebikade, E. O.; Gottlieb, E. R.; Ajao, O.; Benali, M.; Vlachos, D. G.; Ierapetritou, M.; Epps, T. H., III Ambient-pressure lignin valorization to high-performance polymers by intensified reductive catalytic deconstruction. *Sci. Adv.* **2022**, *8* (3), No. eabj7523.

(32) Chin, K. C. H.; Cui, J.; O'Dea, R. M.; Epps, T. H., III; Boydston, A. J. Vat 3D printing of bioderivable photoresins − toward sustainable and robust thermoplastic parts. *ACS Sustainable Chem. Eng.* **2023**, *11* (5), 1867−1874.

(33) Fredi, G.; Dorigato, A. Recycling of Bioplastic waste: A review. *Adv. Ind. Eng. Polym. Res.* **2021**, *4* (3), 159−177.

(34) Hottle, T. A.; Bilec, M. M.; Landis, A. E. Biopolymer production and end of life comparisons using life cycle assessment. *Resour. Conserv. Recycl.* **2017**, *122*, 295−306.

(35) Coates, G. W.; Getzler, Y. D. Chemical recycling to monomer for an ideal, circular polymer economy. *Nat. Rev. Mater.* **2020**, *5* (7), 501−516.

(36) Parkatzidis, K.; Wang, H. S.; Truong, N. P.; Anastasaki, A. Recent developments and future challenges in controlled radical polymerization: a 2020 update. *Chem* **2020**, *6* (7), 1575−1588.

(37) Holmberg, A. L.; Reno, K. H.; Nguyen, N. A.; Wool, R. P.; Epps, T. H., III Syringyl methacrylate, a hardwood lignin-based monomer for high-T_g polymeric materials. *ACS Macro Lett.* **2016**, *5* (5), 574−578.

(38) Holmberg, A. L.; Nguyen, N. A.; Karavolias, M. G.; Reno, K. H.; Wool, R. P.; Epps, T. H., III Softwood lignin-based methacrylate polymers with tunable thermal and viscoelastic properties. *Macromolecules* **2016**, *49* (4), 1286−1295.

(39) Holmberg, A. L.; Reno, K. H.; Epps, T. H., III Polymers Prepared from Functionalized Dimethoxyphenol Monomers. U.S. Patent US10,253,131, 2019.

(40) Epps, T. H., III; Holmberg, A. L.; Nicastro, K. H.; Wang, S.; Saha, B.; Shuai, L.; Vlachos, D. G.; Morris, M. A. Bio-Based Polymers From Raw Lignocellulosic Biomass. U.S. Patent US20230113164, 2023.

(41) Wang, H. S.; Truong, N. P.; Pei, Z.; Coote, M. L.; Anastasaki, A. Reversing RAFT Polymerization: Near-Quantitative Monomer Generation Via a Catalyst-Free Depolymerization Approach. *J. Am. Chem. Soc.* **2022**, *144* (10), 4678−4684.

(42) Martinez, M. R.; Schild, D.; De Luca Bossa, F.; Matyjaszewski, K. Depolymerization of polymethacrylates by iron ATRP. *Macromolecules* **2022**, *55* (23), 10590−10599.

(43) Young, J. B.; Hughes, R. W.; Tamura, A. M.; Bailey, L. S.; Stewart, K. A.; Sumerlin, B. S. Bulk depolymerization of poly(methyl methacrylate) via chain-end initiation for catalyst-free reversion to monomer. *Chem* **2023**, *9* (9), 2669−2682.

(44) Wallace, W. E.. Mass Spectra. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J.; Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2021.

(45) Demirci, G.; Podkościelna, B.; Bartnicki, A.; Mergo, P.; Gil, M.; Cetinkaya, O.; Gawdzik, B. Copolymerization and thermal study of the new methacrylate derivative of 2,4,6-trichlorophenol. *J. Therm. Anal. Calorim.* **2017**, *127*, 2263−2271.

(46) Kashiwagi, T.; Inabi, A.; Hamins, A. Behavior of primary radicals during thermal degradation of poly(methyl methacrylate). *Polym. Degrad. Stab.* **1989**, *26* (2), 161−184.

(47) Manring, L. E. Thermal degradation of poly(methyl methacrylate). 4. Random side-group scission. *Macromolecules* **1991**, *24* (11), 3304−3309.

(48) Holland, B. J.; Hay, J. N. The effect of polymerisation conditions on the kinetics and mechanisms of thermal degradation of PMMA. *Polym. Degrad. Stab.* **2002**, *77* (3), 435−439.

(49) Hu, Y.-H.; Chen, C.-Y. The effect of end groups on the thermal degradation of poly(methyl methacrylate). *Polym. Degrad. Stab.* **2003**, *82* (1), 81−88.

(50) Peterson, J. D.; Vyazovkin, S.; Wight, C. A. Kinetic study of stabilizing effect of oxygen on thermal degradation of poly(methyl methacrylate). *J. Phys. Chem. B* **1999**, *103* (38), 8087−8092.

(51) Kusenberg, M.; Roosen, M.; Zayoud, A.; Djokic, M. R.; Dao Thi, H.; De Meester, S.; Ragaert, K.; Kresovic, U.; Van Geem, K. M. Assessing the feasibility of chemical recycling via steam cracking of untreated plastic waste pyrolysis oils: feedstock impurities, product yields and coke formation. *Waste Manage.* **2022**, *141*, 104−114.

(52) Sivagami, K.; Kumar, K. V.; Tamizhdurai, P.; Govindarajan, D.; Kumar, M.; Nambi, I. Conversion of plastic waste into fuel oil using zeolite catalysts in a bench-scale pyrolysis reactor. *RSC Adv.* **2022**, *12* (13), 7612−7620.

(53) Kusenberg, M.; Eschenbacher, A.; Djokic, M. R.; Zayoud, A.; Ragaert, K.; De Meester, S.; Van Geem, K. M. Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate? *Waste Manage.* **2022**, *138*, 83−115.

(54) Ellis, L. D.; Rorrer, N. A.; Sullivan, K. P.; Otto, M.; McGeehan, J. E.; Román-Leshkov, Y.; Wierckx, N.; Beckham, G. T. Chemical and biological catalysis for plastics recycling and upcycling. *Nat. Catal.* **2021**, *4* (7), 539−556.

(55) Smolders, K.; Baeyens, J. Thermal degradation of PMMA in fluidised beds. *Waste Manage.* **2004**, *24* (8), 849−857.

(56) Vyazovkin, S.; Burnham, A. K.; Criado, J. M.; Pérez-Maqueda, L. A.; Popescu, C.; Sbirrazzuoli, N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim. Acta* **2011**, *520* (1), 1−19.

(57) Vyazovkin, S.; Wight, C. A. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. *Thermochim. Acta* **1999**, *340−341*, 53−68.

(58) Moens, E. K. C.; De Smit, K.; Marien, Y. W.; Trigilio, A. D.; Van Steenberge, P. H. M.; Van Geem, K. M.; Dubois, J.-L.; D'hooge, D. R. Progress in reaction mechanisms and reactor technologies for thermochemical recycling of poly(methyl methacrylate). *Polymers* **2020**, *12* (8), 1667.

(59) Çaykara, T.; Eroğlu, M. S.; Güven, O. Thermal and oxidative degradation of vinyl triethoxysilane − methyl methacrylate copolymers. *Polym. Degrad. Stab.* **1999**, *63* (1), 65−70.

(60) Jones, G. R.; Wang, H. S.; Parkatzidis, K.; Whitfield, R.; Truong, N. P.; Anastasaki, A. Reversed controlled polymerization (RCP): depolymerization from well-defined polymers to monomers. *J. Am. Chem. Soc.* **2023**, *145* (18), 9898−9915.

(61) Otsu, T.; Yamada, B.; Sugiyama, S.; Mori, S. Effects of ortho-substituents on reactivities, tacticities, and ceiling temperatures of radical polymerizations of phenyl methacrylates. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18* (7), 2197−2207.

(62) Esmizadeh, E.; Khalili, S.; Vahidifar, A.; Naderi, G.; Dubois, C. Waste Polymethyl Methacrylate (PMMA): Recycling and High-Yield Monomer Recovery. In *Handbook of Ecomaterials*; Springer International Publishing: Cham, Switzerland, 2018; pp 1−33.

(63) Godiya, C. B.; Gabrielli, S.; Materazzi, S.; Pianesi, M. S.; Stefanini, N.; Marcantoni, E. Depolymerization of waste poly(methyl methacrylate) scraps and purification of depolymerized products. *J. Environ. Manage.* **2019**, *231*, 1012−1020.

(64) Jakubowski, W.; Matyjaszewski, K. Activators regenerated by electron transfer for atom-transfer radical polymerization of (meth)-acrylates and related block copolymers. *Angew. Chem., Int. Ed.* **2006**, *45* (27), 4482−4486.

(65) Kwak, Y.; Matyjaszewski, K. ARGET ATRP of methyl methacrylate in the presence of nitrogen-based ligands as reducing agents. *Polym. Int.* **2009**, *58* (3), 242−247.

(66) Dayrit, F. M. The properties of lauric acid and their significance in coconut oil. *J. Am. Oil Chem. Soc.* **2015**, *92* (1), 1−15.

(67) Holmberg, A. L.; Reno, K. H.; Wool, R. P.; Epps, T. H., III Biobased building blocks for the rational design of renewable block polymers. *Soft Matter* **2014**, *10* (38), 7405−7424.

(68) Holmberg, A. L.; Stanzione, J. F., III; Wool, R. P.; Epps, T. H., III A facile method for generating designer block copolymers from functionalized lignin model compounds. *ACS Sustainable Chem. Eng.* **2014**, *2* (4), 569−573.

(69) Holden, G.; Bishop, E. T.; Legge, N. R. Thermoplastic elastomers. *J. Polym. Sci., Part C: Polym. Symp.* **1969**, *26* (1), 37−57.

(70) Maji, P.; Naskar, K. Styrenic block copolymer-based thermoplastic elastomers in smart applications: advances in synthesis, microstructure, and structure−property relationships — a review. *J. Appl. Polym. Sci.* **2022**, *139* (39), No. e52942.

(71) Spontak, R. J.; Patel, N. P. Thermoplastic elastomers: fundamentals and applications. *Curr. Opin. Colloid Interface Sci.* **2000**, *5* (5−6), 333−340.

https://doi.org/10.1021/acs.macromol.3c01985
Macromolecules 2023, 56, 9796−9803