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COMMUNICATION

Depolymerizable poly(benzyl ether)-based materials for selective room temperature recycling†

Matthew S. Baker, Hyungwoo Kim, Michael G. Olah, Gregory G. Lewis and Scott T. Phillips*

This communication addresses the question of whether it is possible to design a polymer that can be modified easily to create various traditional classes of polymeric materials while also incorporating a mechanism into the backbone of the polymer for facilitating selective end-of-life recycling capabilities into the new types of materials. We illustrate these capabilities using depolymerizable poly(benzyl ethers), which we modify to access desired properties in plastics. The poly(benzyl ethers) also are designed for selective, programmed, room temperature, and continuous depolymerization of plastics to monomers when the plastic is no longer needed.

Efficient and routine chemical recycling of post-consumer plastics is a major unrealized goal. In the United States, only 8.8% of plastic from municipal waste is recycled.[1] Another 10.6% is incinerated to generate energy, while the remaining material is buried in landfills.[1] The recycled plastic—such as expanded poly(styrene) or poly(ethylene terephthalate)—is processed by mechanical compaction, grinding, and melting to create lower quality plastic containing polymers (often of shorter lengths) as well as various impurities such as dyes, plasticizers, and absorbed organics (particularly when the original plastic contained food).

Pyrolysis, catalyzed hydrolysis, and various nucleophilic substitution reactions have been explored on laboratory scales for chemical recycling of select plastics by converting them into monomers and other small molecules.[2,3] These methods often are limited, however, due to high temperatures involved in the processes, the waste products that are generated, or the inherent instability of the polymers in the presence of water.[3c] For traditional plastics, low recovery rates of useful monomers or small molecules also often limit chemical recycling to laboratory-scale efforts.[3]

Other alternative methods for recycling plastics include (i) designing new separation techniques for purifying solid plastics with different chemical compositions,[5] or (ii) creating new polymers that are purposely designed to revert to small molecules under appropriate conditions. This latter approach typically is based on polymers that convert to small molecules based on dynamic covalent[3,6] and non-covalent bonds,[7] where temperature, concentration, and/or water are used to control the equilibrium between polymerization and degradation.

A complimentary, but distinctly different approach is described in Fig. 1a. We use newly designed, low-ceiling-temperature polymers (poly(benzyl ethers) in this work) not only to yield a desired property in a plastic, but also to enable depolymerization into monomers at room temperature (e.g., 23 °C) exactly when desired based on exposure of the polymers to a specific chemical signal that would not be encountered in normal use. This selective depolymerisation reaction converts a desired polymer into monomers, which overcomes the common difficulty of separating plastics based on differences in density, or polymers based on differences in solubility. We refer to these polymers as CD_r polymers since they undergo **c**ontinuous **d**epolymerization after a **r**eaction-based detection event.[8]

In this communication, we demonstrate synthetic strategies for modifying poly(benzyl ethers) to realize several polymeric materials, and we further show that isolation and repolymerization of the monomers from depolymerized poly(benzyl ethers) yields new, pure polymer, which enables a closed-loop method for recycling plastics. Moreover, the process of depolymerization facilitates separation of various traditional, non-depolymerizable plastics/polymers from those that depolymerize in hypothetical situations that could arise during recycling.

We illustrate these concepts using the polymers in Fig. 1b,[4a] which are a specific type of CD_r polymer that depolymerize through repetitive quinone methide elimination reactions (Fig. 1b). We show that poly(benzyl ethers) are robust polymers, which makes them easy to handle and manipulate into plastics, and we further demonstrate that the

Department of Chemistry, Pennsylvania State University, University Park, PA 16802, USA. E-mail: sphillips@psu.edu

monomers of poly(benzyl ethers) are easily modified to provide access to a variety of polymeric materials (Scheme 1).
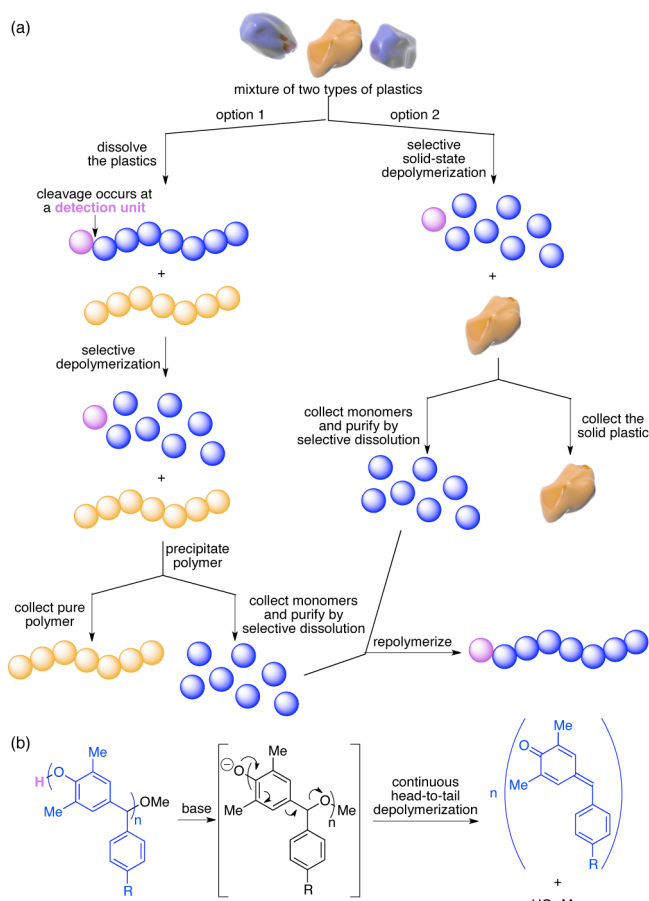

Fig. 1 (a) Two idealized strategies for recycling polymeric materials made from depolymerizable polymers. (b) Self-immolative CD$_r$ poly(benzyl ethers)[4] are used in this work to illustrate the concepts.

Poly(benzyl ethers) are readily accessible through anionic polymerization of quinone methide monomers. Scheme 1a depicts a representative synthesis of one quinone methide monomer used in this study—note the straightforward Fischer esterification reaction that allows incorporation of functionality onto each monomer; this functionality ultimately controls the type of plastic that can be made from each polymer. We prepared monomers **6**–**8** in gram-scale quantities (up to ~10 g) without difficulty. Likewise, the polymerization reaction is straightforward and high yielding (Scheme 1b), and easily provides polymers that contain polar (polymer **10**) or hydrophobic functionality (polymer **11**) on each repeating unit. Appending other functionalities on each repeating unit should be possible as well.

All three poly(benzyl ethers) (**9**–**11** in Scheme 1b) were designed to depolymerize into monomers in response to base since they are terminated with a hydrogen atom (see the phenol in Scheme 1b), although they could be terminated with other functionality that would enable selective depolymerisation to signals such as F$^-$, H$_2$O$_2$, Pd(0), various wavelengths of light, thiols, and others.[4,8] Exposure of polymers **9**–**11** to base (0.5 M 1,8-diazabicyclo[5.4.0]undec-7-

ene (DBU)) in CH$_2$Cl$_2$ at 23 °C,[9] initiates complete depolymerisation to monomers within 1−3 h (ESI Fig. 1†).[10] In the absence of base, however, the polymers are stable when heated to ~200 °C, where the onset of thermal degradation for **9** occurs at 200 °C, **10** at 203 °C, and **11** at 204 °C (ESI Figs. 42−44†).

The modifications on the repeating units, as anticipated, impart unique properties to the polymers. For example, polymer **11**, in comparison to **9** and **10**, is hydrophobic since it contains a fluorinated hydrocarbon attached as an ester to each repeating unit. The water contact angle of paper coated with **11** or **9** illustrates this point: the contact angle for paper coated with **11** is 131° ± 2°, whereas the contact angle for paper coated with **9** is 30° lower (i.e., 98° ± 1°) (ESI Table 1†).
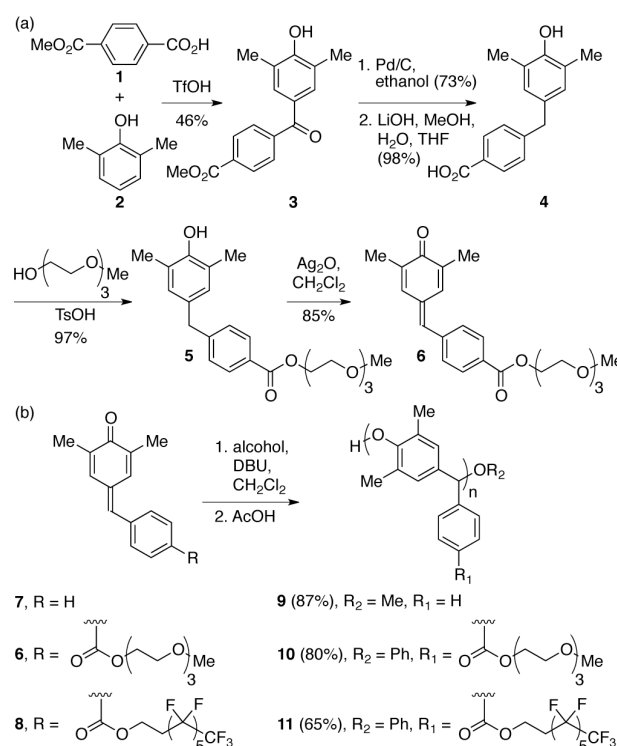
Scheme 1 (a) An example route for preparing quinone methide monomers. (b) Syntheses of three CD$_r$ poly(benzyl ethers).

This trifecta of (i) controlled depolymerization to monomers, (ii) thermal stability, and (iii) straightforward derivatization enables individual testing of each component of the recycling strategies in Fig. 1a. For example, we used polymer **11** to demonstrate recycling option 1. The hydrophobicity of **11** impacts its solubility, giving solubility properties that are similar to poly(styrene). Thus, we simulated recycling option 1 (where two polymers cannot be separated by selective solubility) by treating a THF solution of polymer **11** and poly(styrene) with DBU (0.5 M) at 23 °C. In this context, **11** depolymerized completely in 2 h (ESI Fig. 2†). The resulting monomers (**8**) have substantially different solubility properties compared with poly(styrene) (which was unaffected by DBU,

therefore poly(styrene) was recovered in pure form by selectively precipitating it from the reaction solution (Fig. 2).

Next, we used polymer **10** to illustrate recycling option 2 in Fig. 1a. Polymer **10** can be molded into a desired shape at 90 °C. In this case, we used a U-shaped silicon mold to create a thermoplastic that maintains its shape when handled at room temperature (Fig. 3). Mixing the U-shaped plastic with equally-sized objects shaped as P's and S's (cut from poly(ethylene) and poly(propylene), respectively) in a solution of isopropanol and water creates a demonstration scenario for recycling option 2. In this hypothetical situation, several plastics may have similar solubility properties and density values to one another (or may be laminated together), and therefore would be difficult to separate using conventional techniques, even when crushed into small pieces. However, partial purification of the mixed materials can be achieved by selectively depolymerizing the material made from **10** (i.e., the U) by adding DBU to the solution (Fig. 3), after which the P and the S can be collected easily by filtration. In the absence of DBU, none of the plastic letters change size (second column, Fig. 3), emphasizing that the objects do not dissolve in the solvent in the absence of the applied signal. This ability to depolymerize in the solid state is particularly important for minimizing the use of large volumes of organic solvent that would be needed to dissolve the plastics before separating them, as well as to minimize the consumption of energy that would be required to dissolve the polymers by heating the solutions.

The second stages of both recycling options 1 and 2 (Fig. 1a) involve recovery and repolymerization of poly(benzyl ether) monomers. To demonstrate this concept, we depolymerized **9** (10 µM) in CH_2Cl_2 containing DBU (1.8 mM), which yielded quinone methide monomers.[4a] Recovery of these monomers by washing the CH_2Cl_2 solution with water, evaporating the CH_2Cl_2, and then selectively re-dissolving the quinone methide (**7**) in hot hexanes provided **7** in 26% yield,[11] but with sufficient purity to enable repolymerization to regenerate **9** in 83% yield (ESI Fig. 3†). For comparison, the first synthesis of **9**, using freshly prepared monomer, proceeded in 87% yield. We did not optimize the recovery of **7**,[11] but we anticipate that minor changes to the recovery procedure will increase the yield of recovered **7** substantially.[11]

Taken together, these three individual demonstrations of separation and recycling suggest the feasibility of poly(benzyl ethers) (and, perhaps, other CD_r polymers) to enable the general strategies in Fig. 1a for chemical recycling of plastics, perhaps even when plastics are components of larger composite materials such as laminates, or when mechanical separation of comingled materials is not possible.

Conclusions

This diversity of recycling options, combined with the ease of synthesis and straightforward derivatization of poly(benzyl ethers) to create various polymeric materials, places CD_r poly(benzyl ethers) in a unique position to serve as a starting point for purposely designing plastics that effectively balance function with end-of-use recycling strategies. The scope of this
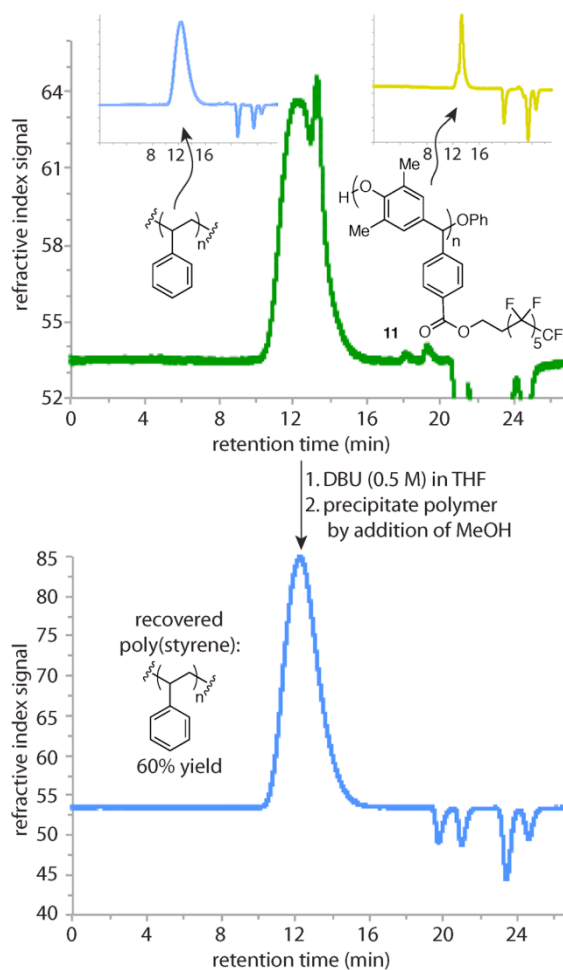

Fig. 2 Separating polymers with similar solubility properties by depolymerizing poly(benzyl ether) **11**. Poly(styrene) (top blue GPC chromatogram) and **11** (yellow chromatogram) were combined in THF (green chromatogram) and then separated by adding DBU to the solution. ^{1}H NMR spectra corresponding to each step are provided in ESI Fig. 2†.

approach broadens when one considers that CD_r poly(benzyl ethers) are not limited to responding to base; in previous work,[4] we demonstrated that the polymers can be end-capped with detection units that respond to specific applied signals, such as fluoride, Pd(0), or UV light. Such end caps should expand the applications of CD_r poly(benzyl ethers) in the context of recyclable plastics, since some applications may require materials that are stable even to base, while other recycling scenarios may necessitate sequential, selective depolymerization to enable complete separation and recovery of multiple polymers in a mixture, or of composite materials.

Looking broadly, this work illustrates a design principle for new generations of polymeric materials in which polymers are designed both for desirable bulk material properties and for ease of recycling and purification based on a selective, room-temperature head to tail depolymerisation reaction.

Because this is a proof-of-concept study, the demonstration polymers (i.e., functionalized poly(benzyl ethers)) and polymeric materials certainly are not competitive with existing polymeric materials in terms of intrinsic

properties. However, further development of these poly(benzyl ether)-based materials is on-going with the goal of optimizing desired properties and fully characterizing the mechanical, optical, and thermal properties of the materials.

The time horizon for implementation of these concepts likely is long (e.g., tens of years), and ultimately may emerge first in specialized applications. Whether the concepts are ever applied to commodity polymers depends on a variety of factors, including (i) available supplies of raw starting materials, (ii) cost of purification and recycling efforts, and (iii) increased knowledge of the impact of plastic pollution on the health of humans and the environment. However, one thing is certain: the preferred chemical compositions and desired functions of polymeric materials continue to change over time. At some point, theses requirements may match the results of this work, and thus this work could provide a foundation upon which function and recycling will both be given equal consideration at the design stage of a new polymer.

Acknowledgements

Notes and references

1 (a) N. J. Themelis and C. Mussche, *2014 Energy and Economic Value of Municipal Solid Waste (MSW), Including Non-Recycled Plastics (NRP), Currently Landfilled in the Fifty States*, Technical Report to the American Chemistry Council, Columbia University Earth Engineering Center, New York, 2014; (b) T. E. Long, *Science*, 2014, **344**, 706–707.

2 (a) D. S. Achilias, *Material Recycling – Trends and Perspectives*; InTech, Rijeka, Croatia, 2012; (b) I. A. Ignatyev, W. Thielemans and B. Vander Beke, *ChemSusChem*, 2014, **7**, 1579–1593; (c) K. Fukushima, J. M. Lecuyer, D. S. Wei, H. W. Horn, G. O. Jones, H. A. Al-Megren, A. M. Alabdulrahman, F. D. Alsewailem, M. A. McNeil, J. E. Rice and J. L. Hedrick, *Polym. Chem.*, 2013, **4**, 1610–1616.

3 (a) A. A. Garforth, S. Ali, J. Hernández-Martínez and A. Akah, *Curr. Opin. Solid State Mater. Sci.*, 2004, **8**, 419–425; (b) H. Nishida, *Polym. J.*, 2011, **43**, 435–447; (c) The following reference describes an example of a chemically recyclable polymer that is not susceptible to hydrolysis: Y. Ishido, A. Kanazawa, S. Kanaoka and S. Aoshima, *Polym. Chem.*, 2014, **5**, 43–47.

4 (a) M. G. Olah, J. S. Robbins, M. S. Baker and S. T. Phillips, *Macromolecules*, 2013, **46**, 5924–5928; (b) K. Yeung, H. Kim, H. Mohapatra, S. T. Phillips, *J. Am. Chem. Soc.*, 2015, **137**, 5324–5327.

5 A. Winkleman, R. Perez-Castillejos, K. L. Gudiksen, S. T. Phillips, M. Prentiss and G. M. Whitesides, *Anal. Chem.*, 2007, **79**, 6542–6550.

6 (a) S. W. Craig, J. A. Manzer and E. B. Coughlin, *Macromolecules*, 2001, **34**, 7929–7931; (b) T. Endo and D. Nagai, *Macromol. Symp.*, 2005, **226**, 79–86; (c) D. J. Darensbourg, A. D. Yeung and S. H. Wei, *Green Chem.*, 2013, **15**, 1578-1583; (d) C. E. Diesendruck, G. I. Peterson, H. J. Kulik, J. A. Kaitz, B. D. Mar, P. A. May, S. R. White, T. J. Martínez, A. J. Boydston and J. S. Moore, *Nat. Chem.*, 2014, **6**, 623–628; (e) J. M. García, G. O. Jones, K. Virwani, B. D.
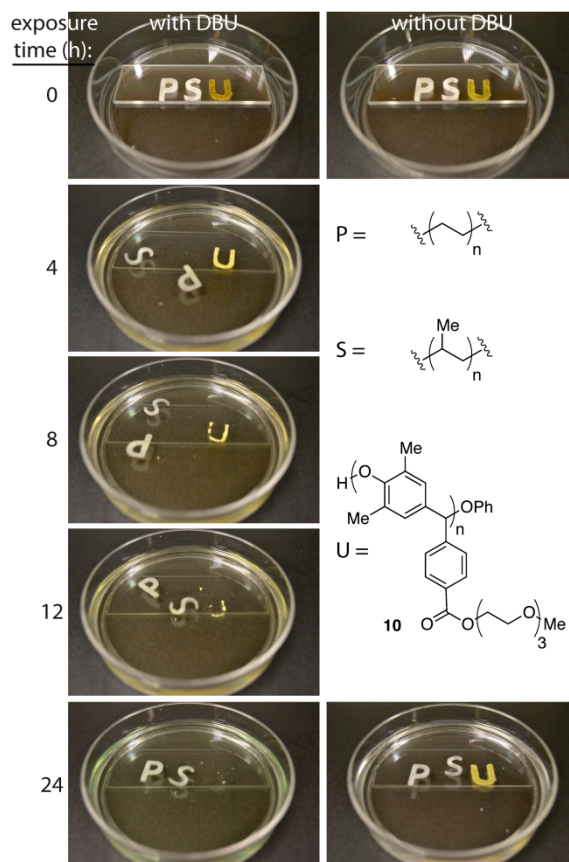
Fig. 3 Separation of solid poly(ethylene) (P) and solid poly(propylene) (S) from solid poly(benzyl ether) **10** (U) by selective depolymerization of **10** via exposure of all solids to a 1:3 *i*-PrOH–H$_2$O solution containing DBU (0.5 M) at 23 °C. Approximately 80 mg of **10** was used to make one of the 1.1 cm-wide × 1.4 cm-tall × 1.8 mm-thick U's.

Mccloskey, D. J. Boday, G. M. Huurne, H. W. Horn, D. J. Coady, A. M. Bintaleb, A. M. S. Alabdulrahman, F. Alsewailem, H. A. A. Almegren and J. L. Hedrick, *Science*, 2014, **344**, 732–735; (f) H. Ying, Y. Zhang and J. Cheng, *Nat. Commun.*, 2014, **5**, 3218; (g) A. M. DiLauro, G. G. Lewis and S. T. Phillips, *Angew. Chem. Int. Ed.*, 2015, **127**, 6298–6303; (h) H. Ying and J. Cheng, *J. Am. Chem. Soc.*, 2014, **136**, 16974–16977; (i) S. Rajendran, R. Raghunathan, I. Hevus, R. Krishnan, A. Ugrinov, M. P. Sibi, D. C. Webster and J. Sivaguru, *Angew. Chem. Int. Ed.*, 2015, **54**, 1159–1163.

7 (a) T. Takata, *Polym. J.*, 2006, **38**, 1–20; (b) T. Aida, E. W. Meijer and S. I. Stupp, *Science*, 2012, **335**, 813–817; (c) J. R. Kumpfer, J. J. Wie, J. P. Swanson, F. L. Beyer, M. E. Mackay and S. J. Rowan, *Macromolecules*, 2012, **45**, 473–480.

8 (a) S. T. Phillips and A. M. DiLauro, *ACS Macro Lett.*, 2014, **3**, 298–304; (b) G. I. Peterson, M. B. Larsen and A. J. Boydston, *Macromolecules*, 2012, **45**, 7317–7328; (c) S. Gnaim and D. Shabat, *Acc. Chem. Res.*, 2014, **47**, 2970–2984; (d) A. P. Esser-Kahn, S. A. Odom, N. R. Sottos, S. R. White and J. S. Moore, *Macromolecules*, 2011, **44**, 5539–5553; (e) Self-immolative polymers represent the first examples of CD$_r$ polymers: A. Sagi, R. Weinstain, N. Karton and D. Shabat, *J. Am. Chem. Soc.*, 2008, **130**, 5434–5435.

9 Trifluorobenzene was used as the solvent for **11**.

10 Previously,[4a] we demonstrated that poly(benzyl ethers) that are end-capped with acetate do not depolymerize in response to base. Therefore, the base response in this work arises from the terminal phenol in the CD$_r$ poly(benzyl ethers).

11 We did not attempt to improve the yield of recovered **7** since our primary goal was to demonstrate that **7** could be

isolated with sufficient purity to enable repolymerization. However, we note that clean depolymerization of poly(benzyl ethers) to monomers occurs in dry solvent.[4a] Thus, minimizing exposure of monomers to water will minimize hydration of quinone methides and likely will improve the yield of recovered monomer. Commercial applications of CD$_r$ poly(benzyl ethers) will provide the motivation to devise improved recovery procedures for quinone methide monomers.

Table of contents

Straightforward modifications to quinone methide monomers creates self-immolative poly(benzyl ethers) that enable room temperature separation and recycling of plastics.