Closing the Loop for Benzylic Polyacylhydrazone(PAcHy) Soft Materials

Matthew B. Minus[a]*, Chukwuzubelu Okenwa Ufodike[b,c,d]*, Al Mazedur Rahman[e], Evan McHenry[a], Marco D. Giles[a], Gaius Chukwuka Nzebuka[b]

[a]Department of Chemistry, Prairie View A&M University, 100 University Drive, Prairie View TX 77446 United States

[b]Department of Engineering Technology and Industrial Distribution, Texas A&M University, 3367 TAMU, College Station, TX 77843 United States

[c]Department of Mechanical Engineering (J. Mike Walker '66), Texas A&M University, College Station, TX 77843, United States

[d]Department of Multidisciplinary Engineering, Texas A&M University, College Station, TX 77843, United States

[e]Department of Industrial & Systems Engineering, Texas A&M University, College Station, TX 77843, United States

*Corresponding authors.
Matthew B. Minus. E-mail: maminus@pvamu.edu
Chukwuzubelu Okenwa Ufodike. E-mail: ufodike@tamu.edu

1 Abstract

The earth faces a pressing environmental challenge with the annual pollution of millions of tons of plastic waste. This issue is exacerbated by the inherent characteristics of plastics, including their high thermal stability and low biodegradability. In response, the scientific community has dedicated significant efforts to combat plastic pollution and develop environmentally sustainable soft materials. A promising approach is the creation of soft materials that can be efficiently recycled within a closed-loop system, thereby minimizing their chemical impact on the environment. This study introduces polyacylhydrazones as a novel class of soft materials with the potential for closed-loop recycling. Closed-loop polymers are sought after as sustainable materials of the future. Dynamic covalent polymers have the potential to act as closed-loop materials because of their reversible linkages. However, only a few materials currently exist.[1–3] Polyacylhydrazones have been explored as dynamic covalent polymers with multiple uses. Herein we demonstrate the first study that shows their potential as closed-loop materials. We show synthetic techniques that produce

1

14 hydrophobic polyacylhydrazones with unique length and morphology under kinetic control. Fi-
15 nally, we show the facile decomposition of a benzylic hydrazone bond down to monomeric units
16 and extraction-based separation, without the need for chromatography. This work advances our
17 understanding of these innovative materials and validates benzylic polyacylhydrazones as "closed-
18 loop" materials for a more sustainable future.
19

21 **Graphical Abstract**
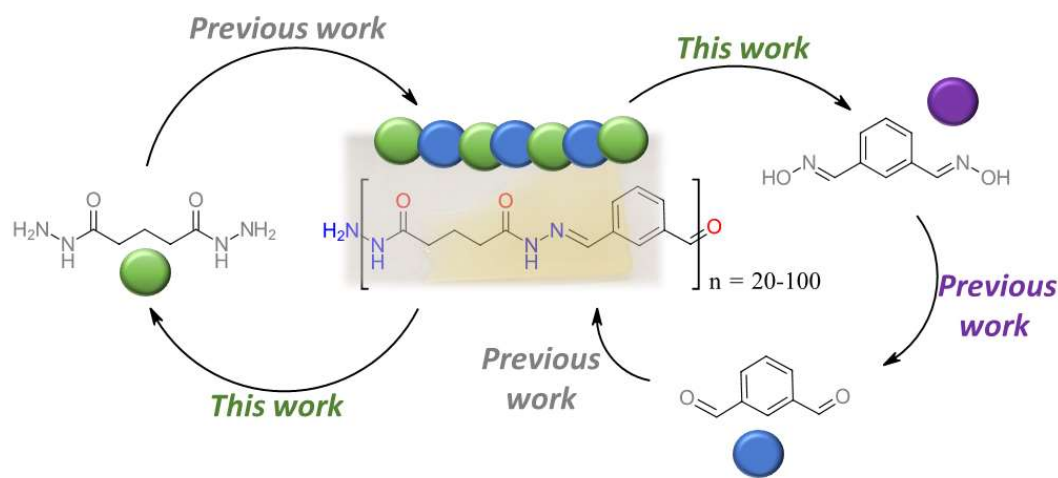
1. Introduction

25 Over the past decade, extensive research efforts have been dedicated to unraveling the far-reaching
26 consequences of plastic pollution [4,5]. Alarming statistics underscore the severity of the issue, with
27 approximately 29 million tons of plastic waste being disposed of annually in the United States
28 alone [5,6]. This unrelenting influx of new plastic waste, compounded by the absence of controlled
29 decomposition pathways [7], has created a crisis that imperils the existence of countless marine spe-
30 cies [8,9]. Given that marine organisms constitute a substantial portion of our global protein supply,
31 this crisis transcends ecological concerns, extending into the realm of food security and potential
32 humanitarian catastrophes [10]. The gravity of the situation is further exacerbated by the role of mi-
33 croplastics, originating from common plastic additives like bisphenol A (BPA) [11] and Perfluoroal-
34 kyl Substances (PFAS), in endocrine disruption and the proliferation of estrogen-dependent

2

35   cancers [12]. To combat the plastic pollution crisis, a coalition of chemists, biochemists, and engi-

36   neers has rallied to develop technologies aimed at mitigating the millions of tons of plastic waste

37   generated annually [6,13]. While existing approaches such as catalytic degradation and solvent sepa-

38   ration methods show promise [14,15], a broader array of strategies is required to create future materi-

39   als with minimal environmental impacts [16,17]. The emergence of biodegradable materials like pol-

40   ylactic acid (PLA) represents a step in the right direction [18]. However, the proliferation of PLA,

41   without a concurrent diversification of biodegradable plastics, may inadvertently bestow an evo-

42   lutionary advantage upon bacteria capable of digesting them [19,20]. This looming challenge under-

43   scores the urgent need for a two-fold approach: **(1)** A diverse array of biodegradable plastics that

44   must be made and dumped in a way that feeds environmental bacteria proportionally; **(2)** The

45   reverse engineering of materials, enabling selective degradation and reusability, thereby achieving

46   a net zero chemical impact on the environment. Consequently, there is a growing interest within

47   the scientific community in the development of materials that mimic plastic properties while being

48   amenable to "closed-loop" recycling. [1,21]

49   Previous research achievements have indicated that plastics featuring dynamic covalent bonds pos-

50   sess the inherent potential for "closed-loop" recycling [22,23]. Among these dynamic covalent bonds,

51   the acylhydrazone linkage has emerged as a promising dynamic covalent polymer system[24]. While

52   polyacylhydrazones have more recently gained recognition for their role in the development of

53   crosslinked soft materials and hydrogels [25], our study presents, the pioneering synthesis of hydro-

54   phobic hydrolytically stable polyacylhydrazones through condensation in dimethyl sulfoxide

55   (DMSO). The simplicity of the benchtop synthesis process is elucidated, along with some potential

56   applications of these materials. Most significantly, we unveil the selective conditions conducive to

57   the degradation of these polymers to the monomeric units. We also demonstrate the extraction-

58   based separation of monomer units, closing the loop for benzylic polyacylhydrazones. In this con-

59   text, these findings could help the efforts towards addressing the pressing problem of plastic pol-

60   lution and contribute to the creation of environmentally responsible materials.

61

2. Results and discussion

We began our studies with an interest in creating hydrophobic, water-stable, degradable materials. Polyacylhydrazones were appealing as sustainable polymers because several papers reported the reversibility of the acylhydrazone bond.[26–28] Polyacylhydrazones have a long history of being used as hydrophilic polymers. These studies demonstrate their robust polymerization along with their hydrolytic stability at neutral pHs. Furthermore, polyacylhydrazones are known to be water-stable from their uses in protein chemistry.[29] Therefore, we started our project by targeting a few hydrazone polymers with potentially hydrophobic properties. Additionally, previous research has shown differences in kinetic exchange between different ketones and aldehydes with hydrazides.[30] Exchange rate difference could prove critical for potential decomposition pathways. Therefore, commercially available aliphatic and benzylic diketones/dialdehydes that could produce hydrophobic materials with different decomposition kinetics were chosen (**Figure 1**, Materials A-C). Dialdehyde monomers (**a**, **b**, and **c**) were coupled with the dihydrazide monomer (**1**) (**Figure 1**). The reaction was then transferred to a silicon mold and dried in the fume hood at 60 °C. As shown in **Figure 1**, the resulting materials gave drastically different physical appearances. **Material A** gave the appearance of a deep-brown material. This is likely due to enolate/enol formation that is common with beta keto aldehydes, esters, and ketones. In contrast, **Material B** had a semi-transparent amber appearance and easily took the shape of the cast when dried. **Material C** formed a less flexible semi-transparent material that also took the shape of its silicon mold. This preliminary screening underscores the profound impact that the choice of dialdehyde monomer can exert on the resulting properties of these polyacylhydrazone block polymer systems. This small group of polymers demonstrated that different materials can be generated just by changing the dialdehyde of these polyacylhydrazone polymer systems. This initial investigation into the synthesis of polyacylhydrazone-based materials not only underscores the diversity of materials that can be generated within the polyacylhydrazone framework but warrants further exploration into the structure-property relationships of this class of materials.

https://doi.org/10.26434/chemrxiv-2024-078mj **ORCID:** https://orcid.org/0000-0002-6534-538X Content not peer-reviewed by ChemRxiv. **License:** CC BY-NC-ND 4.0
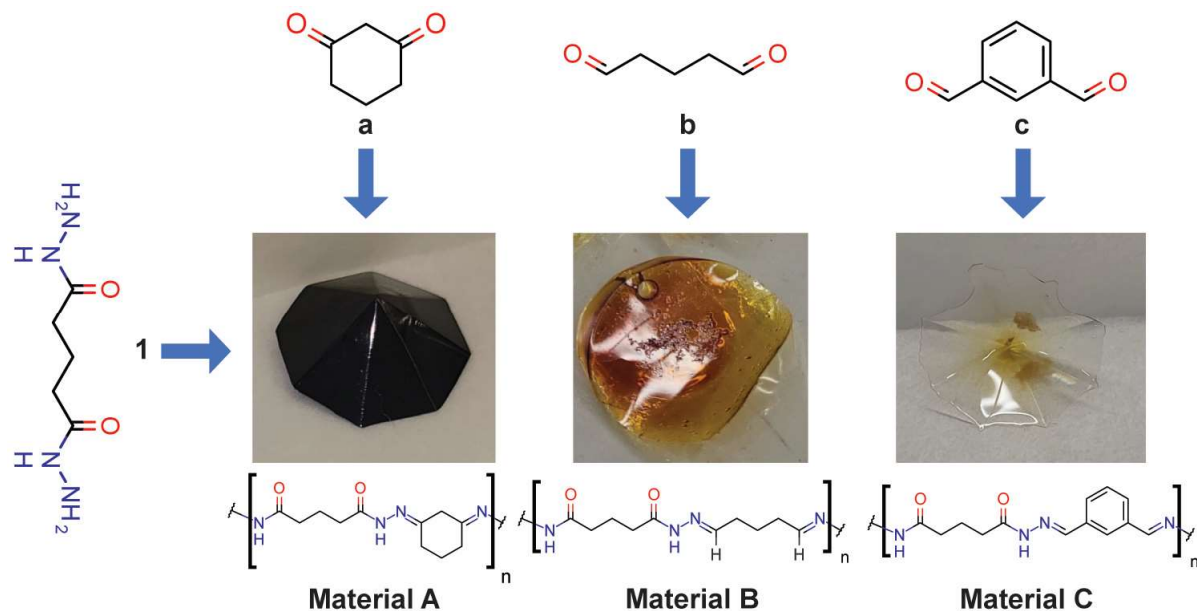
Figure 1. Dihydrazide (**1**) is combined with dialdehydes (**a-c**) at 0.2 M concentration in 10% AcOH in DMSO. Reactions are then solvent casted in silicon molds to form **Materials A-C**.

2.1. Solvent Casting vs. Precipitation

We noticed that the material properties we witnessed did not match the powdery materials that were previously reported in literature.[24] In our quest for a deeper understanding of the solvent casting effect on polymer properties, we embarked on a comparative study, pitting our solvent casting methodology (performed at 60 °C in a fume hood, (**Figure 2a**) against a precipitation method (**Figure 2c**) mentioned in the literature [24]. In our hands the precipitation method aggregated while drying, creating a porous morphology for the polyacylhydrazones (**Figure 2d**). In contrast the solvent casting method created a smoother continuous surface morphology (**Figure 2b**). This comparative analysis not only underscores the profound influence of drying methodology on the resulting polymer morphology but also hints at the potential role of drying conditions in shaping the material's physical attributes.

5

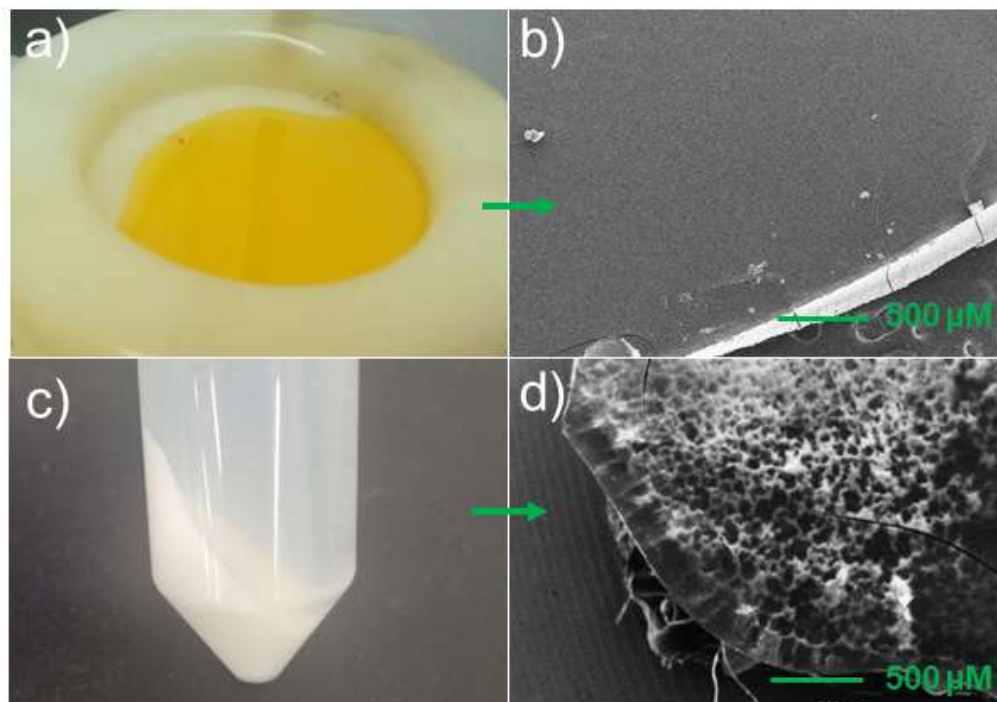**Figure 2. (a)** *New Method* - The reaction mixture for polymer **Material C** is condensed on a silicon mold **(b)** Once dried, the resulting material, **Material C**, is taken from the silicon mold and imaged by SEM **(c)** *Previous method* - **Material C** is precipitated from the reaction mixture, filtered, and left at room temperature to dry **(d)** once dried, the precipitated **Material C** is imaged by SEM.

101

102

2.2. Effect of Reaction Concentration and DMSO

Materials B and **C** were previously reported in situ in literature.[24] However, we noticed that the plastic and film-like properties that we saw were not mentioned (**Figure 1**). Furthermore, the morphologies appeared to be different due to our drying method (**Figure 2**). We suspected the slow condensation of the living polymers (Materials A-C) in (10%AcOH in DMSO) caused further *in situ* reactivity of the polymers. Furthermore, the remaining concentrations of DMSO (10 % w/w) resulted in the smooth and flexible materials that were witnessed. Therefore, we investigated the effect of concentration on polymerization. **Material C** was the only one that could be completely reconstituted in DMSO or DMF after condensation. As a result, the polymerization of **Material C** was monitored at several different concentrations by GPC (**Figure 3a**). It was seen that all

6

113   reactions halted within 24 hours, reaching a kinetic limit at each concentration. Additionally, plot-

114   ting the log of the reaction concentration vs. the M_W of the polymer shows a direct correlation

115   between reaction concentration and polymer size **(Figure 3b)**. We hypothesize that as concentra-

116   tion increases, the polymer size increases, and the effective concentration of the reactive ends de-

117   creases. Eventually, the reactive ends are too far away to collide with each other at the reaction

118   temperature and concentration, causing the polymerization to stop. Polymers formed and dried at

119   different concentrations show different molecular weights and appearances (**Figure 3**, inset). This

120   data is important because it suggests that even though the polyacylhydrazone polymerization is

121   reversible and thermodynamically controlled at higher temperatures, the polymer mass can be con-

122   centration-dependent at lower temperatures (< 60 °C). This discovery suggests that the molecular

123   weight of the polymers can be controlled beyond at lower temperatures.
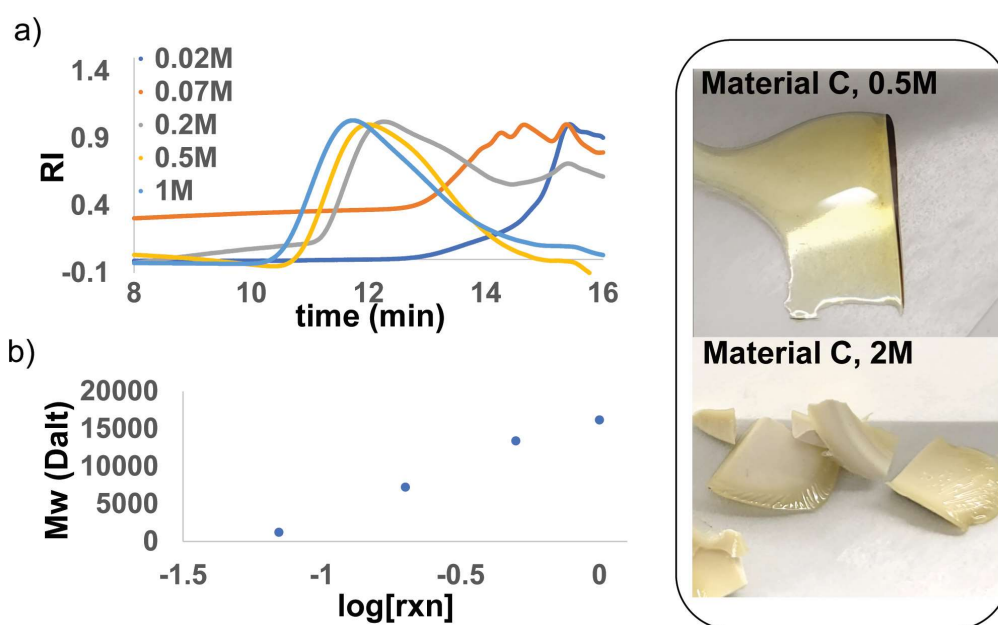

Figure 3. (a) GPC traces of **Material C** under polymerization conditions at different con-

centrations **(b)** M_w as determined by GPC is plotted against the log of the reaction con-

centration (log[rxn]) (Inset) **Material C** is solvent casted after being synthesized at 0.5M

(top) and 2M (bottom) concentrations.

124

7

2.3. End Capping: Controlling molecular mass

Next, our focus shifted towards gaining control of the polymer size by capping the reactive end with a terminal monomer. It is well known that molecular weight and morphology play a critical role in material properties. Therefore, being able to control the polymer size for each material would allow for a wider range of potential properties and applications. We envisioned capping the polymer with a terminal hydrazide to create controlled access to smaller oligomers (**Figure 4a**). Literature suggests that aldehyde and ketone exchange does not readily occur until 100 °C.[24] However, hydrazine and hydrazide exchange seemed to readily occur around 50 °C. Therefore, we chose to use benzoic hydrazide, because it could readily exchange with **Materials A-C** at mild temperatures. When incubated with benzoic hydrazide **Materials A** and **B** were not soluble in 10% AcOH/DMSO. Over time **Material A** was partially dissolved, and partially exchanged with benzoic hydrazide in 10% AcOH/DMSO. However, **Material B** remained insoluble, barely exchanging with benzoic hydrazide. **Material C** was soluble in DMSO. Therefore, the effects of hydrazide end capping could only be assessed by GPC for **Materials A and C**.

GPC analysis of **Materials A and C** showed a significant difference in end capping response between materials. The DMSO soluble **Material C** exhibited different molecular weights that were dependent upon the concentration of benzoic hydrazide added (**Figure 4b-c**). **Material A** responded differently to benzoic hydrazide. The solution-soluble components of end-capped **Material A** did not vary in mass depending on benzoic hydrazide concentration (**Figure S2**). Instead, the appearance of a low molecular weight compound (≤ 1kD) only increased with increasing benzoic hydrazide (**Figure S2**). This data suggests that once soluble **Material A** quickly breaks down into small molecular weight oligomers. Based upon these results we can conclude that a hydrazide end capping strategy can help to control molecular weight, but the success of this strategy is dependent upon the structure of the parent polymer chain. While the terminal hydrazide strategy was effective for controlling the molecular weight of the benzoic polyacylhydrazone **Material C**, it was ineffective for accessing different molecular weights of aliphatic aldehyde and ketone-based polyacylhydrazones, **Materials A and B**.
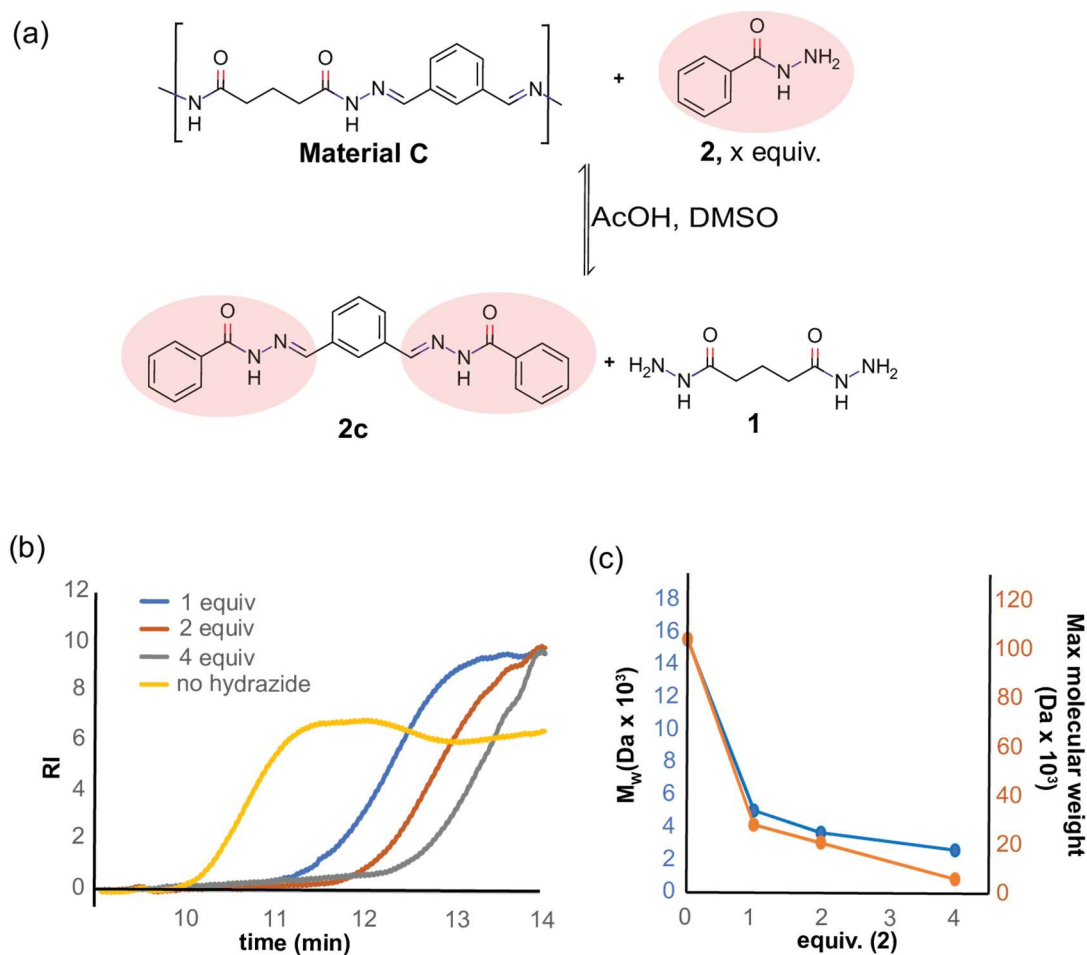
8

Figure 4. (a) Cartoon of terminal hydrazide exchanging with the dihydrazide 1 in Material C **(b)** GPC traces of **Material C** after 14 h reaction with **2**. **(c)** M_w and Max molecular weight (orange) are plotted against equivalents of hydrazide used in the decomposition re-
~~action.~~

2.4. Degradation

The potential success of terminal hydrazide capping strategies highlights the dynamic nature of polyacylhydrazones at low temperatures (< 50 °C) with excess terminal hydrazide. As forementioned, we were interested in utilizing the dynamic nature of closed-loop recycling. We envisioned using a terminal nucleophile to degrade these polymers down to monomer units and then separate them (**Figure 5a**). Previous kinetic studies conducted by the Raines group showed that hydroxyl-amine is 100 times faster at breaking existing hydrazone bonds than acyl hydrazide.[31]

9

160   Hydroxylamine is also terminal because the hydroxyl side of the molecule cannot form hydrazone

161   bonds. Therefore, we investigated the degradative capacity of hydroxylamine with **Materials A-**

162   **C** (**Figure 5a**). **Materials A-C** were incubated with hydroxylamine HCl with 10% AcOH in

163   DMSO as the solvent and monitored over time by NMR (**Figure 5b**). After 10 minutes of incuba-

164   tion, the NMR peaks for **Material C** became narrower for both the aromatic and aliphatic regions

165   (**Figure 5b-c**). In addition, the oxime peaks appeared around 8.1 ppm (**Figure 5b**). Both the nar-

166   rowing of NMR peaks and the emergence of oxime peaks suggested that depolymerization was

167   occurring.

168   Although Material C demonstrated rapid decomposition under DMSO conditions, the decomposi-

169   tions of **Materials A and B** were not as fast. **Material A** completely dissolved over time (48 h).

170   Peak overlap between the diketone and dihydrazide monomers of **Material A** prevented clear

171   NMR analysis of decomposition. **Material B** would not dissolve in solution even after 48 h of

172   incubation with excess hydroxylamine. We can conclude that the complete decomposition to mon-

173   omers did not happen for **Material B** because the monomers for **Material B** are soluble in DMSO.

174   These results highlight that the structure of the dialdehyde and diketone monomer significantly

175   affects the material's response to hydroxylamine-based degradation conditions.
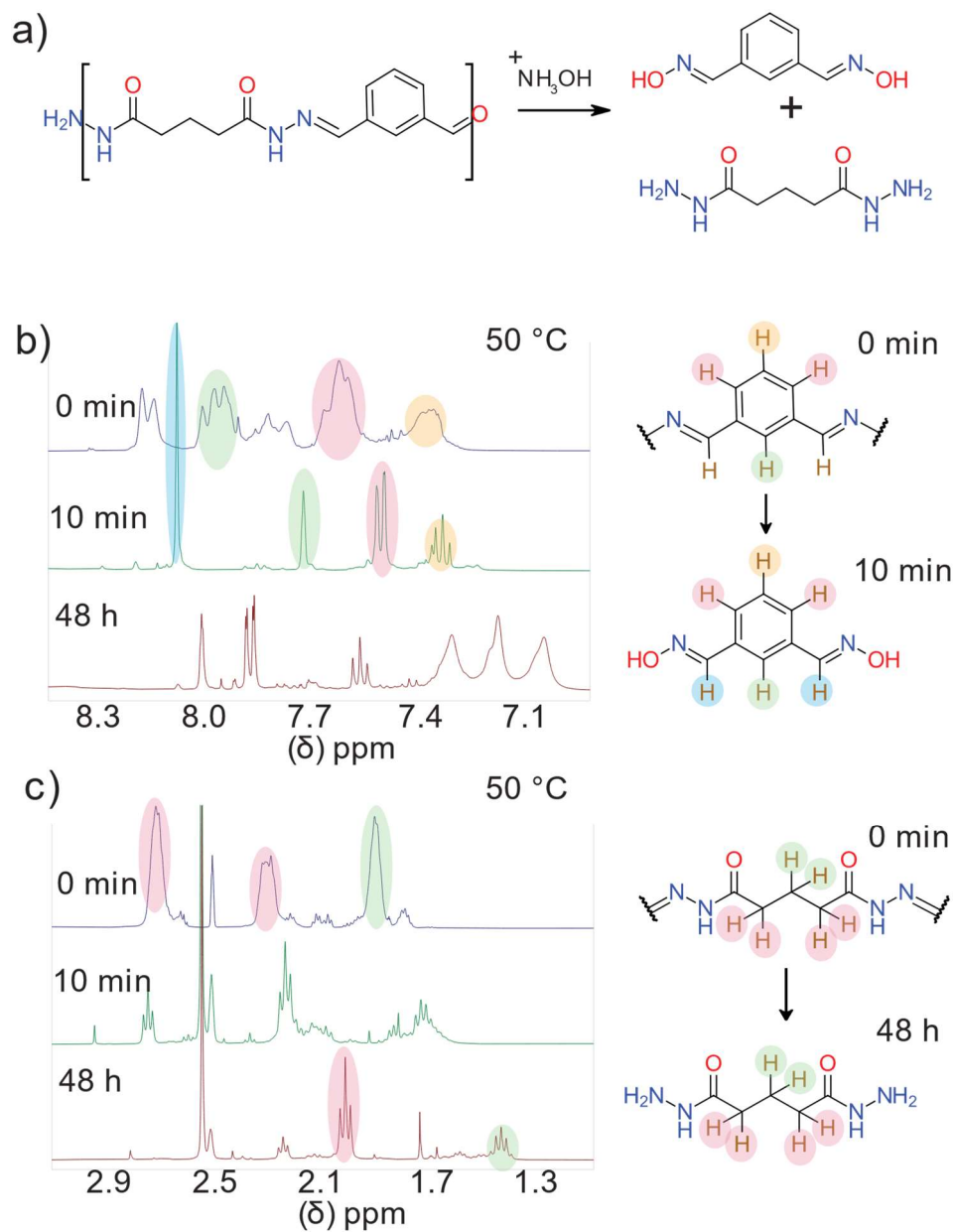
Figure 5. (a) Material C completely decomposes into monomeric units. **(b)** aromatic region (8.4 to 7.0 ppm) is monitored as **Material C** decomposes over time. **(c)** aliphatic region (3.0 to 1.2 ppm) is monitored as **Material C** decomposes over time.

176

177   **2.5. Isolation**

178   Once it was clear that we could achieve degradation for **Materials A and C**. We strove to separate

179   the degradation monomers through a simple extraction process. We first optimized degradation to

180   use 20% H_2O in MeCN as a solvent system instead of DMSO, because MeCN is easier to remove

11

181   by vacuum. Incubation of **Material C** for 24 h at 37 °C resulted in the generation of the desired

182   dioxime product while **Material A** failed to undergo complete decomposition. Through solvent

183   screening, it was found that **3c** dissolved in CH_2Cl_2 while the pentane dihydrazide was insoluble.

184   Therefore, we performed extractions of the decomposed mixtures with CH_2Cl_2(**Figure 6b**). NMR

185   results show a preferential removal of **3c** by CH_2Cl_2washing. After 6 washes a small amount of **3c**

186   remained (**Figure 6c**). After 12 washes only **1** remained in the aqueous solution. Analysis of the

187   CH_2Cl_2 extract shows that only **3c** was carried into the CH_2Cl_2 layer **(Figure S3)**. These results

188   demonstrate that can **Material C** be completely broken down into small molecules. However, the

189   resulting small molecules can be easily separated without the need for chromatography. The hy-

190   drolysis of oximes to aldehydes is well-established in literature. Therefore, by decomposing the

191   polymer into monomeric units and separating the monomers through extraction the recycling loop

192   for this benzylic polyacylhydrazone, **Material C,** was closed through this study. Future research

193   must be done to establish how general this finding is for different benzylic polyacylhydrazones.

194   Being encouraged by the extraction-based separation of **Material C** decomposition products, we

195   were interested in the extraction of the **Material A** decomposition products. Material A was also

196   incubated in the 20% H_2O solution with 4 equivalents of hydroxylamine HCl for 24 h. After 24 h,

197   some insoluble material remained in solution. This result suggests that the decomposition of **Ma-**

198   **terial A** once again was less robust than the decomposition of **Material C**. Additionally only a

199   small portion (<10%) of diketone could be extracted by CH_2Cl_2. This poor extraction suggests

200   incomplete decomposition because 1,3-cyclohexanediooxime is soluble in CH_2Cl_2. In previous

201   studies, the aliphatic ketone forms a more stable hydrazone than the aliphatic aldehyde with slower

202   kinetics.[26] This study shows that the benzylic hydrazone is less stable than both the aliphatic

203   diketone and dialdehyde-based hydrazones in the presence of strong nucleophiles.
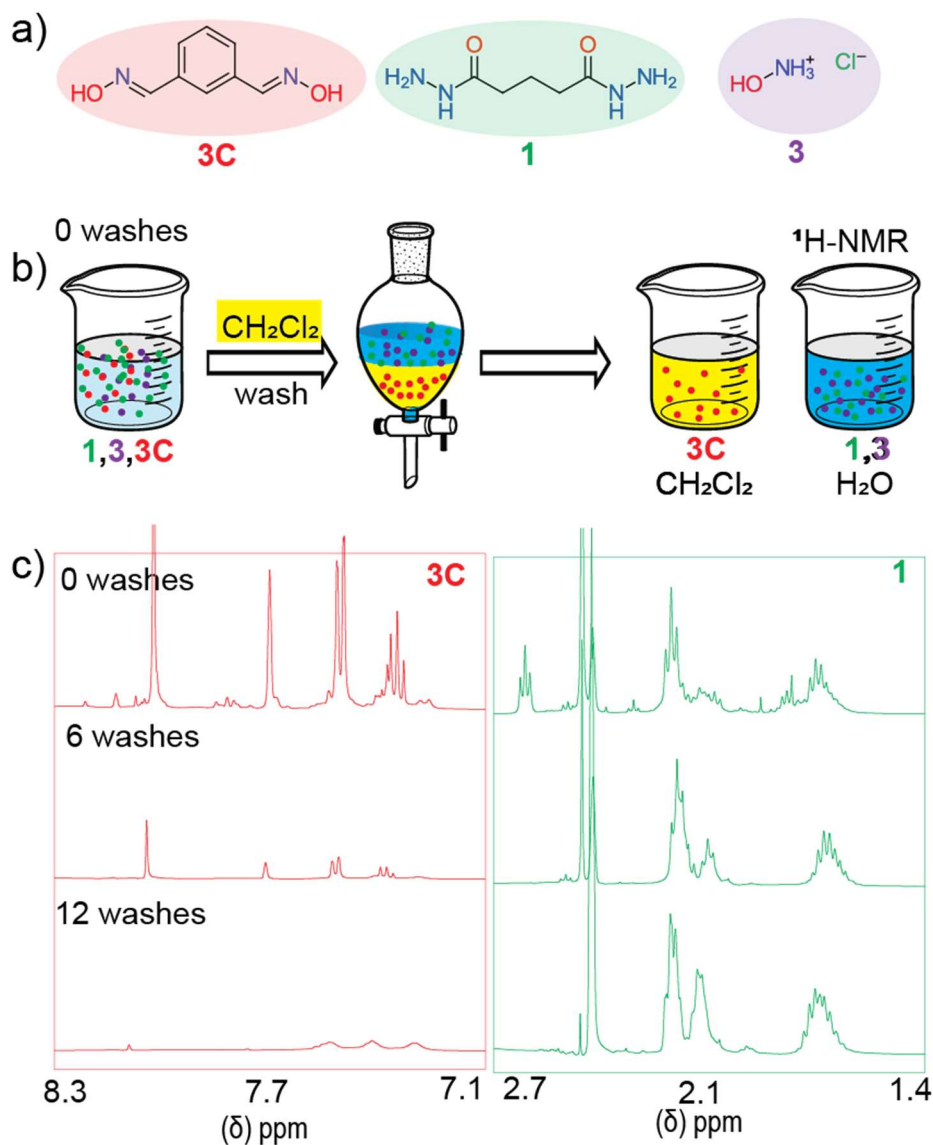
12

Figure 6. **(a)** molecules in crude decomposition mixture of **Material C (b)** cartoon of extraction-based separation of **3c** from monomer 1. **(c)** NMR of crude decomposition mixture before, during, and after CH_2Cl_2 extractions. Small molecule **3c** disappears from aqueous solution after consecutive CH_2Cl_2 washing.

204

205

3. Conclusion: An advance in Sustainable Materials

207

208   The creation of more sustainable materials is a pressing concern for the survivability of the

209 current ecosystem, this research in combination with previous studies highlights polyacylhydrazone materials as useful dynamic covalent polymers with the potential for sustainability. We

13

discovered that the condensation of polyacylhydrazones in dimethyl sulfoxide (DMSO) yields soft polyacylhydrazones with different morphologies than the previously reported materials due to their retention of DMSO during the drying process. We show that polymer size can be controlled with the stoichiometric addition of terminal hydrazide.

In our opinion, the most important discovery of this work lies in the validation of a benzylic polyacylhydrazone as a "closed-loop" material. We have demonstrated their degradability under mild reaction temperatures (37 - 50°C). We have shown that acylpolyhydrazones with benzylic hydrazone linkages can be decomposed to monomer using hydroxylamine HCl in just 10 minutes. We have also shown that the resulting dioxime and dihydrazide products can be separated with simple extraction methods. Pairing these new results with previous chemical methods[24,32] affirms the candidacy of benzylic polyacylhydrazones for large-scale "closed-loop" recycling.

In the wake of this research, our future endeavors are poised to delve deeper into the intricate structure-property relationships of these materials. Through a better structure property understanding we aim to unlock their potential as recyclable plastics that seamlessly integrate with emerging manufacturing technologies, including 3D printing. Additionally, we look forward to expanding the potential for closed-loop recycling to more benzylic and aliphatic polyacylhydrazones, thus increasing the scope of polyacylhydrazones with the potential for "closed-loop" recycling.

Credit authorship contribution statement

Matthew B. Minus: Conceptualization, Investigation, Methodology, Modeling, Simulation, Formal analysis, Validation, Software, Data curation, Visualization, Writing - original draft, Writing – review & editing, Supervision, Project administration, Resources. **Chukwuzubelu Okenwa Ufodike:** Conceptualization, Investigation, Methodology, Modeling, Simulation, Formal analysis, Validation, Software, Data curation, Visualization, Writing - original draft, Writing – review & editing, Supervision, Project administration, Resources. **Al Mazedur Rahman:** Experimentation, Formal analysis. **Evan McHenry:** Experimentation, Formal analysis, **Marco D. Giles:** Methodology, Experimentation, Formal analysis. **Gaius Chukwuka Nzebuka:** Conceptualization, Data curation, Visualization

14

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. However, the instruments at Prairie View used for these experiments were purchased with grant funding from the US Department of Education Title III Grant: P031E200044.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We thank Professor Ufodike Research Group (PURG), and the Digital Manufacturing & Distribution Lab (DMD-Lab) at Texas A&M Engineering Experiment Station, Texas A&M University, College Station, TX. We also thank the Minus and Giles Research Group at the PVAMU Chemistry Department. Lastly, we thank the Dow Sure program for supporting the Research efforts of Evan McHenry.

Appendix

260

References

(1) Christensen, P. R.; Scheuermann, A. M.; Loeffler, K. E.; Helms, B. A. Closed-Loop Recycling of Plastics Enabled by Dynamic Covalent Diketoenamine Bonds. *Nat. Chem.* **2019**, *11* (5), 442–448. https://doi.org/10.1038/s41557-019-0249-2.

(2) Yuan, X.; Bank, M. S.; Sonne, C.; Ok, Y. S. Dual Closed-Loop Chemical Recycling Support Sustainable Mitigation of Plastic Pollution. *Matter* **2021**, *4* (4), 1095–1097. https://doi.org/10.1016/j.matt.2021.03.014.

(3) Clarke, R. W.; Sandmeier, T.; Franklin, K. A.; Reich, D.; Zhang, X.; Vengallur, N.; Patra, T. K.; Tannenbaum, R. J.; Adhikari, S.; Kumar, S. K.; Rovis, T.; Chen, E. Y.-X. Dynamic Cross-linking Compatibilizes Immiscible Mixed Plastics. *Nature* **2023**, *616* (7958), 731–739. https://doi.org/10.1038/s41586-023-05858-3.

(4) Ahmed, T.; Shahid, M.; Azeem, F.; Rasul, I.; Shah, A. A.; Noman, M.; Hameed, A.; Manzoor, N.; Manzoor, I.; Muhammad, S. Biodegradation of Plastics: Current Scenario and Future Prospects for Environmental Safety. *Environ. Sci. Pollut. Res.* **2018**, *25* (8), 7287–7298. https://doi.org/10.1007/s11356-018-1234-9.

(5) Cressey, D. Bottles, Bags, Ropes and Toothbrushes: The Struggle to Track Ocean Plastics. *Nature* **2016**, *536* (7616), 263–265. https://doi.org/10.1038/536263a.

(6) MacLeod, M.; Arp, H. P. H.; Tekman, M. B.; Jahnke, A. The Global Threat from Plastic Pollution. *Science* **2021**, *373* (6550), 61–65. https://doi.org/10.1126/science.abg5433.

(7) Tokiwa, Y.; Calabia, B. P.; Ugwu, C. U.; Aiba, S. Biodegradability of Plastics. *Int. J. Mol. Sci.* **2009**, *10* (9), 3722–3742. https://doi.org/10.3390/ijms10093722.

(8) Penn, J. L.; Deutsch, C. Avoiding Ocean Mass Extinction from Climate Warming. *Science* **2022**, *376* (6592), 524–526. https://doi.org/10.1126/science.abe9039.

(9) Eriksen, M.; Lebreton, L. C. M.; Carson, H. S.; Thiel, M.; Moore, C. J.; Borerro, J. C.; Galgani, F.; Ryan, P. G.; Reisser, J. Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea. *PLOS ONE* **2014**, *9* (12), e111913. https://doi.org/10.1371/journal.pone.0111913.

(10) Mora, C.; Myers, R. A.; Coll, M.; Libralato, S.; Pitcher, T. J.; Sumaila, R. U.; Zeller, D.; Watson, R.; Gaston, K. J.; Worm, B. Management Effectiveness of the World's Marine Fisheries. *PLOS Biol.* **2009**, *7* (6), e1000131. https://doi.org/10.1371/journal.pbio.1000131.

(11) Gould, J. C.; Leonard, L. S.; Maness, S. C.; Wagner, B. L.; Conner, K.; Zacharewski, T.; Safe, S.; McDonnell, D. P.; Gaido, K. W. Bisphenol A Interacts with the Estrogen Receptor α in a Distinct Manner from Estradiol. *Mol. Cell. Endocrinol.* **1998**, *142* (1), 203–214. https://doi.org/10.1016/S0303-7207(98)00084-7.

(12) Gao, H.; Yang, B.-J.; Li, N.; Feng, L.-M.; Shi, X.-Y.; Zhao, W.-H.; Liu, S.-J. Bisphenol A and Hormone-Associated Cancers: Current Progress and Perspectives. *Medicine (Baltimore)* **2015**, *94* (1), e211. https://doi.org/10.1097/MD.0000000000000211.

(13) Khoaele, K. K.; Gbadeyan, O. J.; Chunilall, V.; Sithole, B. The Devastation of Waste Plastic on the Environment and Remediation Processes: A Critical Review. *Sustainability* **2023**, *15* (6), 5233. https://doi.org/10.3390/su15065233.

(14) Du, H.; Wang, Q.; Chen, G.; wang, J. Photo/Electro-Catalytic Degradation of Micro- and Nano-Plastics by Nanomaterials and Corresponding Degradation Mechanism. *TrAC Trends Anal. Chem.* **2022**, *157*, 116815. https://doi.org/10.1016/j.trac.2022.116815.

(15) A. Petersen, H.; T. Myren, T. H.; J. O'Sullivan, S.; R. Luca, O. Electrochemical Methods for Materials Recycling. *Mater. Adv.* **2021**, *2* (4), 1113–1138. https://doi.org/10.1039/D0MA00689K.

(16) Zhao, Y.-B.; Lv, X.-D.; Ni, H.-G. Solvent-Based Separation and Recycling of Waste Plastics: A Review. *Chemosphere* **2018**, *209*, 707–720. https://doi.org/10.1016/j.chemosphere.2018.06.095.

(17) Ügdüler, S.; Van Geem, K. M.; Roosen, M.; Delbeke, E. I. P.; De Meester, S. Challenges and Opportunities of Solvent-Based Additive Extraction Methods for Plastic Recycling. *Waste Manag.* **2020**, *104*, 148–182. https://doi.org/10.1016/j.wasman.2020.01.003.

(18) Rosenboom, J.-G.; Langer, R.; Traverso, G. Bioplastics for a Circular Economy. *Nat. Rev. Mater.* **2022**, *7* (2), 117–137. https://doi.org/10.1038/s41578-021-00407-8.

(19) Bandini, F.; Vaccari, F.; Soldano, M.; Piccinini, S.; Misci, C.; Bellotti, G.; Taskin, E.; Cocconcelli, P. S.; Puglisi, E. Rigid Bioplastics Shape the Microbial Communities Involved in the Treatment of the Organic Fraction of Municipal Solid Waste. *Front. Microbiol.* **2022**, *13*.

(20) Atiwesh, G.; Mikhael, A.; Parrish, C. C.; Banoub, J.; Le, T.-A. T. Environmental Impact of Bioplastic Use: A Review. *Heliyon* **2021**, *7* (9). https://doi.org/10.1016/j.heliyon.2021.e07918.

(21) Lei, Z.; Chen, H.; Luo, C.; Rong, Y.; Hu, Y.; Jin, Y.; Long, R.; Yu, K.; Zhang, W. Recyclable and Malleable Thermosets Enabled by Activating Dormant Dynamic Linkages. *Nat. Chem.* **2022**, *14* (12), 1399–1404. https://doi.org/10.1038/s41557-022-01046-4.

(22) van Dijken, D. J.; Kovaříček, P.; Ihrig, S. P.; Hecht, S. Acylhydrazones as Widely Tunable Photoswitches. *J. Am. Chem. Soc.* **2015**, *137* (47), 14982–14991. https://doi.org/10.1021/jacs.5b09519.

(23) Socea, L.-I.; Barbuceanu, S.-F.; Pahontu, E. M.; Dumitru, A.-C.; Nitulescu, G. M.; Sfetea, R. C.; Apostol, T.-V. Acylhydrazones and Their Biological Activity: A Review. *Molecules* **2022**, *27* (24), 8719. https://doi.org/10.3390/molecules27248719.

(24) Skene, W. G.; Lehn, J.-M. P. Dynamers: Polyacylhydrazone Reversible Covalent Polymers, Component Exchange, and Constitutional Diversity. *Proc. Natl. Acad. Sci.* **2004**, *101* (22), 8270–8275. https://doi.org/10.1073/pnas.0401885101.

(25) Apostolides, D. E.; Patrickios, C. S. Dynamic Covalent Polymer Hydrogels and Organogels Crosslinked through Acylhydrazone Bonds: Synthesis, Characterization and Applications. *Polym. Int.* **2018**, *67* (6), 627–649. https://doi.org/10.1002/pi.5554.

(26) Levrand, B.; Ruff, Y.; Lehn, J.-M.; Herrmann, A. Controlled Release of Volatile Aldehydes and Ketones by Reversible Hydrazone Formation – "Classical" Profragrances Are Getting Dynamic. *Chem. Commun.* **2006**, No. 28, 2965–2967. https://doi.org/10.1039/B602312F.

(27) Deng, Y.; Zhang, Q.; Qu, D.-H.; Tian, H.; Feringa, B. L. A Chemically Recyclable Crosslinked Polymer Network Enabled by Orthogonal Dynamic Covalent Chemistry. *Angew. Chem.* **2022**, *134* (39), e202209100. https://doi.org/10.1002/ange.202209100.

(28) Psarrou, M.; Kothri, M. G.; Vamvakaki, M. Photo- and Acid-Degradable Polyacylhydrazone–Doxorubicin Conjugates. *Polymers* **2021**, *13* (15), 2461. https://doi.org/10.3390/polym13152461.

(29) King, T. P.; Zhao, S. W.; Lam, T. Preparation of Protein Conjugates via Intermolecular Hydrazone Linkage. *Biochemistry* **1986**, *25* (19), 5774–5779. https://doi.org/10.1021/bi00367a064.

17

348   (30) Kool, E. T.; Park, D.-H.; Crisalli, P. Fast Hydrazone Reactants: Electronic and Acid/Base
349   Effects Strongly Influence Rate at Biological pH. *J. Am. Chem. Soc.* **2013**, *135* (47), 17663–
350   17666. https://doi.org/10.1021/ja407407h.
351   (31) Kalia, J.; Raines, R. T. Hydrolytic Stability of Hydrazones and Oximes. *Angew. Chem. Int.*
352   *Ed.* **2008**, *47* (39), 7523–7526. https://doi.org/10.1002/anie.200802651.
353   (32) Chandrasekhar, S.; Gopalaiah, K. Effective 'Non-Aqueous Hydrolysis' of Oximes with Iodic
354   Acid in Dichloromethane under Mild, Heterogeneous Conditions. *Tetrahedron Lett.* **2002**, *43*
355   (22), 4023–4024. https://doi.org/10.1016/S0040-4039(02)00710-4.
356
357
358