

# Carbon-Resource Recovery from Vinyl Polymers of Cyclic Ketene Acetal Esters Using High-Temperature Water

Yasuhiro Kohsaka<sup>\*a,b</sup>, Akane Kazama<sup>b</sup>, Keigo Matsuo<sup>b</sup>, Shigeru Deguchi<sup>c</sup>, Mitsumasa Osada<sup>b\*</sup>

<sup>a</sup> Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4-17-1 Wakasato, Nagano, Nagano 380-8553, Japan.

<sup>b</sup> Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan.

<sup>c</sup> Research Center for Bioscience and Nanoscience, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan

**Keywords:** Dehydroaspirin, main-chain scission, polymer degradation, hydrolysis, chemical recycling, retro-Kolbe-Schmitt reaction, salicylic acid, phenol, hydrothermal reaction

**Abstract:** Vinyl polymer prepared from 2-methylene-4H-benzo[d][1,3]dioxin-4-one (MBDO), a cyclic ketene acetal ester, is a chemically recyclable polymer that is hydrolyzed to salicylic acid

(SA) and acetic acid (AA). Despite this potential, the polymer, poly-MBDO required a strong acid or base in organic solvent for the hydrolysis. In this study, we report the quantitative conversion of poly-MBDO to phenol by treatment in high-temperature water. Hydrolysis of poly-MBDO afforded SA, which underwent rapid decarboxylation to phenol. For example, poly-MBDO quantitatively afforded phenol upon heating in water at 300 °C for 5 min and freeze-drying. Although the hydrolysis of the main chain was incomplete, the products were volatile and removed by drying the reaction mixture, leaving the residue of pure phenol. Since SA is industrially synthesized from phenol and CO<sub>2</sub>, the synthesis of poly-MBDO from phenol is in principle possible. The quantitative conversion of poly-MBDO to phenol can also be considered as upcycling, since phenol is a raw material for various fine chemicals.

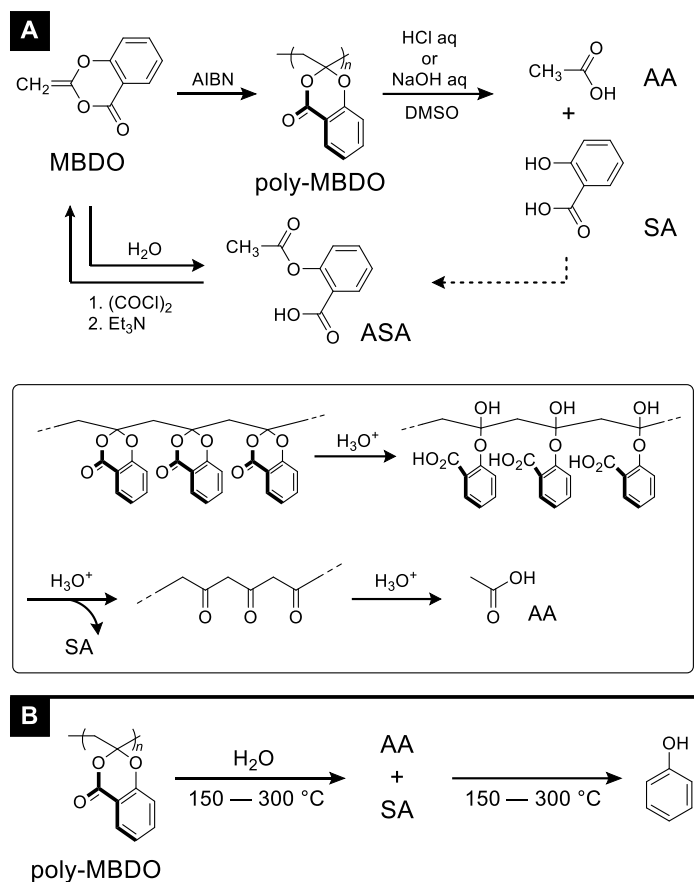
## Introduction

Marine pollution caused by plastic waste and the threat of future depletion of fossil resources have forced fundamental changes in the polymer materials that humans have developed over the past 100 years. For example, carbon resource circulation based on chemical recycling of polymeric materials is recognized as the most important issue to ensure sustainability.<sup>1,2</sup> Chemical recycling is a resource circulation method that consists of polymer degradation into monomers and repolymerization. Since the recovery of high-purity monomers provides high-quality recycled polymers, chemical recycling is recognized as an ideal resource circulation scheme for polymer materials. Numerous efforts have been made to explore polymer structures suitable for chemical recycling and to establish methodologies for recovering monomers from polymers.<sup>3-6</sup>

Depolymerization is a reverse reaction of chain polymerization, in which monomers are continuously eliminated from the polymer chain ends. Because the equilibrium control leads to monomer formation, attention to depolymerization has drastically increased in the past two

decades. Ring-opening polymerization of lactones,<sup>3,7-10</sup> cyclic carbonates,<sup>11</sup> and cyclic acetals,<sup>12,13</sup> which uses reversible bond exchange as the elementary reaction, has a high affinity for chemical recycling. In contrast, the depolymerization of vinyl polymers remains challenging, even though addition polymerization is a reversible process.<sup>14</sup> This is due to the harsh depolymerization conditions owing to the high ceiling temperature of vinyl monomers. Furthermore, depolymerization reactions often compete with side reactions, such as termination and chain-transfer reactions. The exception is polymethacrylates, in which depolymerization affords the corresponding monomer in an almost quantitative yield.<sup>14,15</sup> In other words, depolymerization did not provide sufficient results for other common vinyl monomers.

Main-chain scission (MCS) is a reverse reaction of step-growth polymerization in which polymer chains are sequentially converted into shorter fragments. If selective and quantitative MCS of vinyl polymers is possible, the molecules corresponding to the monomer components should be recovered. Recently, we investigated this concept using the vinyl polymer 2-methylene-4H-benzo[d][1,3]dioxin-4-one (MBDO, **Scheme 1A**).<sup>16,17</sup> MBDO is a cyclic ketene acetal ester derived from acetyl salicylic acid (ASA). Because the hydrolysis of MBDO affords ASA, it is also referred to as ‘dehydroaspirin.’<sup>18</sup> Radical polymerization of MBDO resulted in the corresponding vinyl polymer, poly-MBDO.<sup>16,17</sup> Remarkably, acid and base hydrolysis of poly-MBDO yielded acetic acid (AA) and salicylic acid (SA), suggesting pendant modification and subsequent MCS. This reaction is understandable by the combined hydrolysis of ester, acetal, and 1,3-dicarbonyl skeletons, although the reaction order is unclear. Nevertheless, the overall reaction implies resource circulation, since AA and SA are the starting materials of MBDO.



**Scheme 1. A:** Previous work on recyclable vinyl polymer. **B:** This work.

In practice, the use of recycled AA is probably not valuable because it can be synthesized by fermentation. Rather, the importance of this circulatory system lies in the reuse of SA. The formation of polymerizable double bonds is the most important step in the synthesis of vinyl monomers using sustainable resources. For example, (meth)acryl monomers derived from naturally occurring alcohols are well-known bio-based monomers,<sup>19,20</sup> however, their synthesis requires acrylic acid derivatives, and the production of bio-based acrylic monomers is still in the research stage.<sup>21</sup> In contrast, MBDO is a vinyl monomer derived from SA and AA. The polymerizable double bond is derived as an enol ester, corresponding to AA. Thus, the most significant achievement of our previous report<sup>16</sup> was the discovery that vinyl monomers can be

derived from AA and hydroxycarboxylic acids such as SA. After our first report,<sup>16</sup> a similar molecular design was proposed for other hydroxycarboxylic acids.<sup>22</sup> In these studies, organic solvents and strong reagents, such as sodium hydroxide, were used to recover hydroxycarboxylic acids from vinyl polymers. We envisioned that these vinyl polymers would become truly sustainable if the hydrolysis process for recovering hydroxycarboxylic acid was more environmentally friendly.

High-temperature water has attracted interest from the viewpoint of green chemistry.<sup>23</sup> High-temperature water, that is, water at 100–374 °C and 0.1–22.1 MPa, exhibits a lower dielectric constant and weaker hydrogen bonding.<sup>24–26</sup> Because of these properties, high-temperature water dissolves organic solvents much better than room-temperature water and functions as an excellent medium for organic reactions, including polymer synthesis<sup>27</sup> and degradation.<sup>28</sup> For example, Townsend *et al.* reported the hydrolysis of ether and ester bonds using high-temperature water,<sup>29</sup> while the hydrolysis of poly(ethylene terephthalate) (PET) was investigated for chemical recycling.<sup>30,31</sup> As mentioned above, the degradation of poly-MBDO to AA and SA was proposed to occur via the sequential hydrolysis of acetals, esters, and 1,3-dicarbonyl skeletons. Therefore, the hydrolysis of poly-MBDO with high-temperature water is expected to occur even without organic solvents, acids, or bases, to recover raw materials (**Scheme 1B**). In this study, we investigated the hydrolysis of poly-MBDO in high-temperature water and discussed the reaction mechanism.

## Materials and Methods

**Materials:** Poly-MBDO ( $M_n = 11200$ ,  $D = 1.35$ ) was prepared by radical polymerization, according to our previous report.<sup>16,17</sup> Pure water was prepared using Eliz Essential 3 (Merck). SA, AA, and phenol were purchased from Tokyo Chemical Industry Co Ltd.. Ltd.

**Instruments:** <sup>1</sup>H NMR spectra were recorded in DMSO-*d*<sub>6</sub> using an AVANCE NEO spectrometer (Bruker). The chemical shifts in the <sup>1</sup>H NMR spectra were referenced to the solvent signal. Number-averaged molar mass ( $M_n$ ) and the degree of molar mass dispersity ( $D$ ) were determined by size-exclusion chromatography (SEC) on an EXTREMA chromatograph (JASCO) equipped with two SEC columns [PL-gel, Mixed C (300 mm × 7.5 mm), Polymer Laboratories], using *N,N*-dimethylformamide (DMF, Wako Pure Chemical Industries, for HPLC grade) at 40 °C as an eluent (flow rate: 0.8 mL·min<sup>-1</sup>), and detected with UV (UV-4070, JASCO) and RI (RI-4030, JASCO) detectors. Standard polystyrene (PS) samples (TSK-gel oligomer kit, Tosoh,  $M_p$ :  $1.03 \times 10^6$ ,  $3.89 \times 10^5$ ,  $1.82 \times 10^5$ ,  $3.68 \times 10^4$ ,  $1.36 \times 10^4$ ,  $5.32 \times 10^3$ ,  $3.03 \times 10^3$ ,  $8.73 \times 10^2$  g·mol) were used for calibration. The degradation products were detected by high performance liquid chromatography (HPLC) on an EXTREMA chromatograph (JASCO) equipped with LC columns [InertSustain Phenylhexyl (150 mm × 2.1 mm), GL Science] at 40 °C, using pure water (90 vol%) and acetonitrile (Yoneyama Yakuhin Kogyo Co., Ltd. for LC grade, 10 vol%) mixed with 0.01 wt% trifluoroacetic acid (TFA, Kanto Chemical Co., Inc. for HPLC grade) as the eluent (flow rate: 0.2 mL·min<sup>-1</sup>). The chemicals were detected using a UV detector (UV-4070, JASCO) at 210 and 254 nm.

**Hydrolysis:** Typical procedure. Poly-MBDO (0.100 g, 0.620 mmol) and pure water (2.92 g, 162 mmol) were added to a 6 cm<sup>3</sup> 316-grade stainless-steel tube reactor, which was subsequently immersed in at 150–300 °C sand bath. After 5–360 min, the reactor was removed from the sand bath and rapidly cooled in a water bath. The reaction mixture was diluted to 50 mL in a volumetric

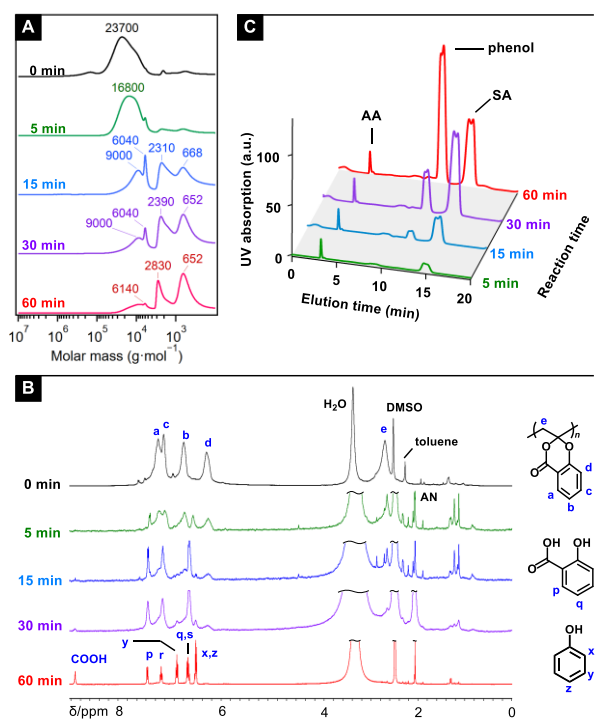
flask using acetonitrile and analyzed by HPLC, as described below. For some entries, the reaction mixture was dried *in vacuo* and the  $^1\text{H}$  NMR spectrum and SEC of the residues were measured.

**Quantification of generated SA, AA, and phenol:** The generated SA, AA, and phenol were quantified using calibration curves for UV absorption at 210 nm observed by HPLC. A series of acetonitrile solutions of SA, and AA in concentrations of 20, 10, 5.0, 2.5, 1.3, and 0.63 mM was analyzed by HPLC. The peaks of SA, AA, and phenol were observed around 15.9, 12.4, and 3.8 min, respectively, and the areas of each peak were plotted with the concentrations to draw calibration lines (**Figure S1**). The concentrations of SA, SS, and phenols generated during poly-MBDO hydrolysis were determined from the calibration lines.

## Results

Poly-MBDO hydrolysis was conducted in a batch-type stainless reaction tube. The reaction tube was immersed in a sand bath at 200 °C for predetermined reaction periods and then rapidly immersed in a water bath. **Figure 1A** shows the changes in SEC curves during the reaction. The broad polymer peak observed at  $23700\text{ g}\cdot\text{mol}^{-1}$  before the reaction gradually shifted to a lower molar mass region. After 15 min, the reaction mixture contained a white powder, probably unreacted Poly-MBDO, whereas that after 30 min did not contain the white powder. Instead, brown and black solids were observed after 30 and 60 min, respectively. Nevertheless, a polymer peak was observed in the SEC curve after 60 min. To detect the products, the reaction mixture was analyzed using  $^1\text{H}$  NMR spectroscopy (**Figure 1B**). Before the reaction started, a signal e around 2.7 ppm assigned to the methylene group in the polymer backbone, was clearly observed. The intensity of signal e decreased after 15 min, whereas a set of sharp aromatic signals, p, q, r, and s, assigned to SA appeared. However, a new set of aromatic signals, that is, signals x and y around

6.7 ppm and z around 7.1 ppm, were observed after 30 min and became stronger after 60 min. These signals were assigned to phenol, suggesting the decarboxylation of SA. **Figure 1C** shows the HPLC profiles of each reaction product. The peak of SA at 15.9 min increased until 30 min, suggesting the hydrolysis of Poly-MBDO, whereas it decreased after 60 min. Instead, the phenol at 12.4 min was observed to be stronger than that of SA. Note that the phenol peak was observed at 15 min, implying decarboxylation from the early stage of the reaction.

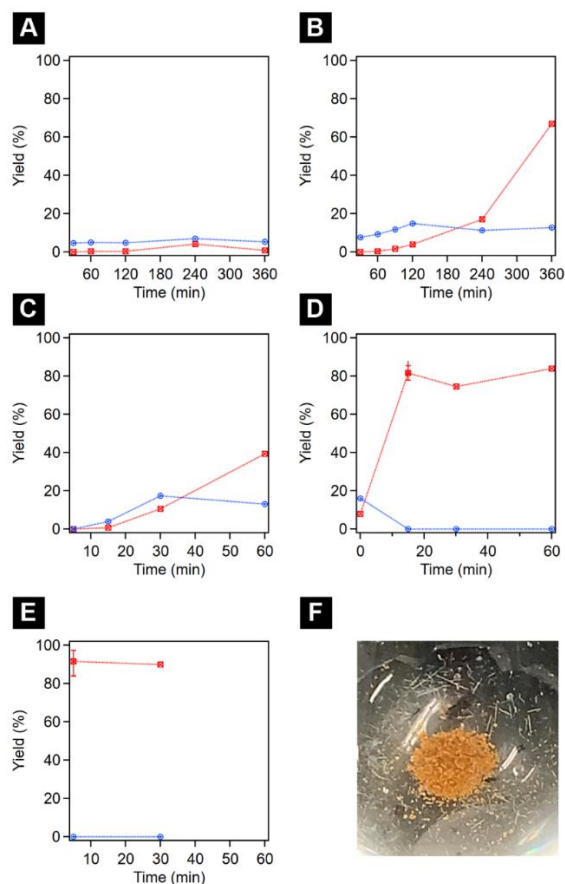


**Figure 1.** Analysis of the hydrolysis products at 200 °C by SEC (**A**, DMF, 40 °C, polystyrene standards), <sup>1</sup>H NMR spectroscopy (400 MHz, DMSO-*d*<sub>6</sub>, 298 K), and HPLC (**C**).

The yields of SA and phenol were estimated from the areas of each UV peak using the calibration lines prepared from SA and phenol solutions at various concentrations (**Figure 2C**). The SA yield was 39% after 60 min, whereas that of phenol was 13%. Therefore, 52% of Poly-MBDO was converted to these compounds, and hydrolysis was incomplete. This observation was in agreement



with the SEC results. Because no distinct peaks, except those of AA, SA, and phenol, were observed in the  $^1\text{H}$  NMR spectrum (**Figure 1B**) and SEC curve (**Figure 1C**), the remaining 41% was anticipated to be insoluble in acetonitrile, a solvent for extraction, or volatile to be removed by drying. The generation of AA by the hydrolysis of the backbone is discussed later.



**Figure 2.** Yield of SA (blue circles) and phenol (red squares) after the hydrolysis at 150 (A), 175 (B), 200 (C), 250 (D), and 300 °C (E). A photograph of products after the hydrolysis for 5 min at 300 °C.

To suppress decarboxylation, hydrolysis was conducted at lower temperatures (150 °C and 175 °C). However, the yield of SA remained at approximately 5% for the treatment at 150 °C, even after 360 min, suggesting low reaction efficiency (**Figure 2A**). The reaction at 175 °C for

360 min afforded SA and phenol in 13% and 67% yields, respectively (**Figure 2B**). Therefore, selective synthesis of SA while avoiding decarboxylation is difficult. Therefore, hydrolysis at higher temperatures was examined to promote the decarboxylation and selective synthesis of phenols. As expected, the reaction at 250 °C for 15 min selectively afforded phenol in a 78–85% yield. Moreover, 5 min was sufficient at 300 °C to obtain phenol in a 84–97% yield. After removing the volatile components from the reaction mixture by drying, phenol was obtained as orange needle-like crystals (**Figure 2E**).

Although phenol was recovered in almost quantitative yield, the yield of AA estimated from HPLC was only 29%. To hydrolyze the main chain to AA, the reaction must undergo an intermediate with a 1,3-dicarbonyl skeleton. A possible reason for the incomplete AA generation is the insufficient hydrolysis of this intermediate to afford precursors such as acetoacetic acid. Furthermore, it has been reported that polyketones containing 1,3-dicarbonyl skeletons are unstable and decompose through various routes.<sup>32</sup> In our previous reports using sodium hydroxide<sup>17</sup> or hydrochloric acid<sup>16</sup> for hydrolysis, AA was selectively obtained because the 1,3-dicarbonyl skeleton was rapidly hydrolyzed. However, if this hydrolysis is slow, side reactions may occur via the polyketones. In fact, in the HPLC profile shown in Fig. 1C, multiple unassignable broad peaks were observed at approximately 10 min. Thus, the MCS did not occur quantitatively, as expected. However, since the only product after drying was phenol, these unexpected products were volatile and were removed from the system along with water and AA.

## Discussion

Focusing on the degradation of pendant groups, that is the hydrolysis of ester and acetal bonds, the product was SA. Because decarboxylation was observed, the total yield of the generated

SA over the reaction should be estimated as the sum of SA and phenol yields. Since hydrolysis was conducted in the presence of much excess water, the reaction should behave as a pseudo-first-order reaction. Therefore, the pendant degradation kinetics can be expressed as follows:

$$[\text{MBDO}]_0 - [\text{SA}] - [\text{phenol}] = [\text{MBDO}]_0 \exp(-kt) \quad (\text{Eq. 1})$$

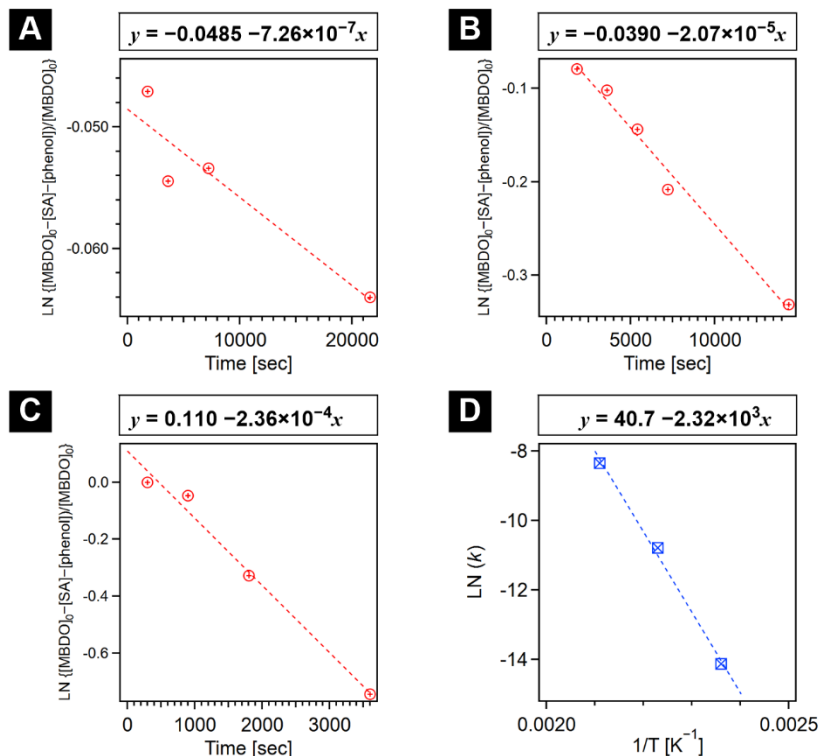
Here,  $[\text{MBDO}]$ ,  $[\text{SA}]$ , and  $[\text{phenol}]$  are the concentrations of MBDO units, SA, and phenol, respectively, and  $[\text{MBDO}]_0$  is the initial concentration of the MBDO unit. where  $k$  is the rate constant and  $t$  is the reaction time. Eq. 1 can be rewritten as follows:

$$\ln\{([\text{MBDO}]_0 - [\text{SA}] - [\text{phenol}])/[\text{MBDO}]_0\} = -kt \quad (\text{Eq. 2})$$

According to Eq. 2, the kinetic plots of pendant degradation are shown in **Figure 3A–C**. The plot for hydrolysis at 150 °C deviated from the approximate line, particularly at the first two points (**Figure 3A**). Generally, it takes time for the internal temperature in the batch-type reaction tube to become constant, and the heat conduction is slower if the bath temperature is lower, that is, the thermal gradient is smaller. The deviations of the first two points were due to this uncontrolled temperature. Nevertheless, the estimated  $k$  value was used for further analysis. The plots for hydrolysis at 175 °C and 200 °C were well fitted to straight lines (**Figure B and C**). The plots for hydrolysis at 250 and 300 °C did not exhibit good linearity due to the saturation of  $[\text{phenol}]$  in the early reaction time. Therefore, the  $k$  values for 150, 175, and 200 °C were plotted according to the Arrhenius equation, Eq. 3 (**Figure 3D**).

$$\ln(k) = \ln(A) - E_a/RT \quad (\text{Eq. 3})$$

where  $A$  is the frequency factor,  $E_a$  is the activation energy, and  $T$  is the absolute temperature. From the slope of the Arrhenius plot,  $E_a$  was estimated as 193 kJ·mol<sup>-1</sup>.



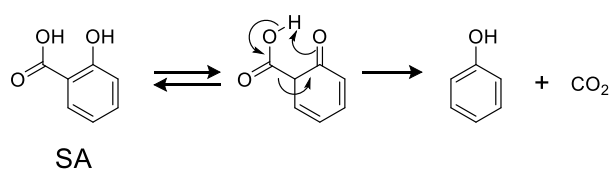
**Figure 3.** Pseudo-first-order kinetic plots for the pendant degradation at 150 (A), 175 (B), and 200 °C (C). Arrhenius plot of pendant degradation (D).

To compare the  $E_a$ s of pendant degradation and decarboxylation of SA, a mixture of SA and water was heated in sand bath and the reaction mixture was analyzed by HPLC. The first-order kinetic plots of decarboxylation at 125–250 °C afforded straight lines (Figure S2A–E). The Arrhenius plot (Figure S2F) afforded an  $E_a$  value of 76.4 kJ·mol<sup>-1</sup>, which was much smaller than that of pendant degradation (193 kJ·mol<sup>-1</sup>). Because the decarboxylation rate was higher than that of pendant degradation, the selective synthesis of SA from poly-MBDO was impossible. In other words, both the hydrolysis and decarboxylation should be promoted to obtain a single product from the aromatic pendants of poly-MBDO.

The slower hydrolysis of poly-MBDO than decarboxylation of SA is attributed to the poor affinity of poly-MBDO to water. The degree of pendant group degradation after heating at 200°C

for 60 min, estimated as the sum of the SA and phenol yields, was 52%. This experimental point exists on the straight line of the pseudo-first-order kinetic plot, suggesting that the reaction mechanisms did not change from the early stage to this stage. On the other hand, regarding the degradation at 250 °C, the pseudo-first-order kinetic constant  $k$  of poly-MBDO was estimated from Arrhenius' equation and  $E_a$  to be  $2.93 \times 10^{-2} \text{s}^{-1}$ . However, that calculated from the first two experimental points was  $1.23 \times 10^{-1} \text{s}^{-1}$ . The reason for larger experimental values than the prediction was attributed to be the change of the rate-determining step. For the hydrolysis above 250 °C, the rate-determining step might not be the polymer dissolution, because water become a less polar solvent with smaller dielectric constant. Furthermore, it is possible that main-chain scission occurred before complete pendant degradation, and the polymer was converted to more hydrophilic fragments. Such changes would cause the change in a rate-determining step. Therefore, heating at higher than 250 °C are effective to convert poly-MBDO into phenol with high selectivity in a shorter time.

In all experiments, the generation of SA followed by the that of phenol, suggesting decarboxylation not from the pendant groups but from SA. Therefore, the decarboxylation can be explained as a retro-Kolbe-Schmidt reaction (**Scheme 2**).



**Scheme 2.** Retro-Kolbe-Schmitt reaction.

## Conclusions

The hydrolysis of poly-MBDO using high-temperature water resulted in the complete degradation of the aromatic pendants into phenol via SA, whereas MCS was incomplete, affording

multiple products, including AA. This behavior is different from that of hydrolysis using strong bases or strong acids, in which AA and SA are selectively obtained. This difference was attributed to the slow hydrolysis of the 1,3-dicarbonyl skeleton.<sup>33</sup> Nevertheless, phenol was recovered in an almost quantitative yield with high purity above 250 °C. In particular, 5 min is sufficient for hydrolysis at 300 °C. The weight-based resource recovery was 53%, whereas the carbon-based resource recovery was 61%.

SA is industrially produced via the Kolbe-Schmidt reaction between phenol and CO<sub>2</sub>.<sup>34</sup> Therefore, it was possible to reproduce SA and poly-MBDO from phenol. Phenol is used as the starting material for the synthesis of various fine chemicals. In this context, poly-MBDO hydrolysis using high-temperature water can be evaluated as poly-MBDO upcycling. The degradation and recycling of vinyl polymers are significant issues, and no effective methods have been established except for the depolymerization of polymethacrylates. The approach proposed in this study, that is, the degradation and upcycling/recycling of vinyl polymers using water, is exciting, and we hope to further advance the establishment of green technology for vinyl polymer circulation by water.

### **Supporting Information.**

The following files are available free of charge.

Calibration lines for AA, SA, and phenol, and kinetic analysis of decarboxylation of SA(PDF).

### **Corresponding Author**

Yasuhiro Kohsaka – Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4-17-1 Wakasato, Nagano, Nagano 380-8553, Japan. Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda,

Nagano 386-8567, Japan. <https://orcid.org/0000-0001-9833-0929>. E-mail: [kohsaka@shinshu-u.ac.jp](mailto:kohsaka@shinshu-u.ac.jp)

Mitsumasa Osada – Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan. <https://orcid.org/0000-0003-3232-5857>; Email: [osadam@shinshu-u.ac.jp](mailto:osadam@shinshu-u.ac.jp)

### **Author Contributions**

YK: Conceptualization, formal analysis, writing - original draft, visualization, supervision, project administration, and funding acquisition. AK: Formal analysis, investigation, resources. km: validation, and investigation. DS: Conceptualization, and writing - review & editing MO: Conceptualization, methodology, writing - review & editing, supervision.

### **Funding Sources**

JSPS KAKENHI Grant Number 23K23397 (for YK), JSPS Grant-in-Aid for JSPS Fellows Grant Number 21J12927 (for AK), and Heisei Memorial Research Grant Program (for YK).

### **Notes**

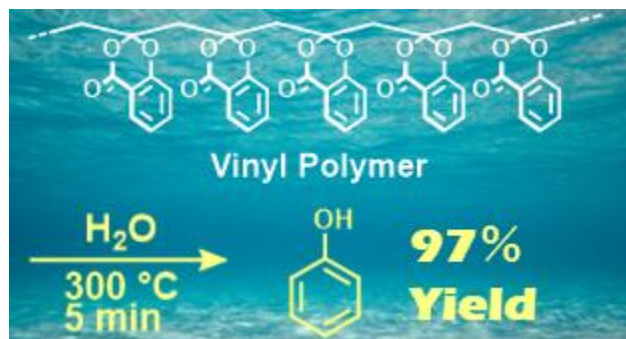
Any additional relevant notes should be placed here.

### **ACKNOWLEDGMENT**

This study was supported by JSPS KAKENHI Grant Number 23K23397 (for YK), JSPS Grant-in-Aid for JSPS Fellows Grant Number 21J12927 (for AK), and Heisei Memorial Research Grant Program (for YK).

### **ABBREVIATIONS**

SA, salicylic acid; AA, acetic acid; MCS, main-chain scission, MBDO, 2-methylene-4H-benzo[d][1,3]dioxin-4-one; Poly-MBDO, vinyl polymer of MBDO; HPLC, high-performance liquid chromatography; SEC, size-exclusion chromatography.



## REFERENCES

- (1) Huang, J.; Veksha, A.; Chan, W. P.; Giannis, A.; Lisak, G. Chemical Recycling of Plastic Waste for Sustainable Material Management: A Prospective Review on Catalysts and Processes. *Renewable Sustainable Energy Rev.* **2022**, *154*, 111866.
- (2) Singh, N.; Ogunseitan, O. A.; Wong, M. H.; Tang, Y. Sustainable Materials Alternative to Petrochemical Plastics Pollution: A Review Analysis. *Sustainable Horizons* **2022**, *2*, 100016.
- (3) Jehanno, C.; Pérez-Madrugal, M. M.; Demarteau, J.; Sardon, H.; Dove, A. P. Organocatalysis for Depolymerisation. *Polym. Chem.* **2018**, *10* (2), 172–186.
- (4) Singer, F. N.; Deacy, A. C.; McGuire, T. M.; Williams, C. K.; Buchard, A. Chemical Recycling of Poly(Cyclohexene Carbonate) Using a Di-MgII Catalyst. *Angew. Chem. Int. Ed Engl.* **2022**, *61* (26), e202201785.
- (5) Kim, J. G. Chemical Recycling of Poly(Bisphenol A Carbonate). *Polym. Chem.* **2020**, *11* (30), 4830–4849.
- (6) Chiba, Y.; Kawatani, R.; Kohsaka, Y. Chemically Recyclable Vinyl Polymers by Free Radical Polymerization of Cyclic Styrene Derivatives. *ACS Macro Lett.* **2023**, *12* (12), 1672–1676.
- (7) Hong, M.; Chen, E. Y. X. Chemically Recyclable Polymers: A Circular Economy Approach to Sustainability. *Green Chem.* **2017**.
- (8) Tang, X. Y.; Hong, M.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y. X. The Quest for Converting Biorenewable Bifunctional Alpha-Methylene-Gamma-Butyrolactone into Degradable and Recyclable Polyester: Controlling Vinyl-Addition/Ring-Opening/Cross-Linking Pathways. *J. Am. Chem. Soc.* **2016**, *138* (43), 14326–14337.
- (9) Zhu, J.-B.; Watson, E. M.; Tang, J.; Chen, E. Y.-X. A Synthetic Polymer System with Repeatable Chemical Recyclability. *Science* **2018**, *360* (6387), 398–403.
- (10) Fahnhorst, G. W.; Hoyer, T. R. A Carbomethoxylated Polyvalerolactone from Malic Acid: Synthesis and Divergent Chemical Recycling. *ACS Macro Lett.* **2018**, *7* (2), 143–147.



- (11) Lamparelli, D. H.; Villar-Yanez, A.; Dittrich, L.; Rintjema, J.; Bravo, F.; Bo, C.; Kleij, A. W. Bicyclic Guanidine Promoted Mechanistically Divergent Depolymerization and Recycling of a Biobased Polycarbonate. *Angew. Chem. Int. Ed Engl.* **2023**, *62* (51), e202314659.
- (12) Shen, T.; Chen, K.; Chen, Y.; Ling, J. Ring-Opening Polymerization of Cyclic Acetals: Strategy for Both Recyclable and Degradable Materials. *Macromol. Rapid Commun.* **2023**, *44* (13), e2300099.
- (13) Takebayashi, K.; Kanazawa, A.; Aoshima, S. Cationic Ring-Opening Copolymerization of a Cyclic Acetal and  $\gamma$ -Butyrolactone: Monomer Sequence Transformation and Polymerization–Depolymerization Control by Vacuuming or Temperature Changes. *Polym. J.* **2023**, *56* (4), 309–317.
- (14) Lohmann, V.; Jones, G. R.; Truong, N. P.; Anastasaki, A. The Thermodynamics and Kinetics of Depolymerization: What Makes Vinyl Monomer Regeneration Feasible? *Chem. Sci.* **2024**, *15* (3), 832–853.
- (15) 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.
- (16) Kazama, A.; Kohsaka, Y. Radical Polymerization of “dehydroaspirin” with the Formation of a Hemiacetal Ester Skeleton: A Hint for Recyclable Vinyl Polymers. *Polym. Chem.* **2019**, *10* (22), 2764–2768.
- (17) Kazama, A.; Kohsaka, Y. Diverse Chemically Recyclable Polymers Obtained by Cationic Vinyl and Ring-Opening Polymerizations of the Cyclic Ketene Acetal Ester “Dehydroaspirin.” *Polym. Chem.* <https://doi.org/10.1039/d2py01181f>.
- (18) Babin, P.; Bennetau, B. 2-Alkylidene-Benzo[1,3]Dioxin-4-Ones: A New Class of Compounds. *Tetrahedron Lett.* **2001**, *42* (31), 5231–5233.
- (19) Techie-Menson, R.; Rono, C. K.; Etale, A.; Mehlana, G.; Darkwa, J.; Makhubela, B. C. E. New Bio-Based Sustainable Polymers and Polymer Composites Based on Methacrylate Derivatives of Furfural, Solketal and Lactic Acid. *Materials Today Communications* **2021**, *28*, 102721.
- (20) Fang, C.; Zhu, X.; Cao, Y.; Xu, X.; Wang, S.; Dong, X. Toward Replacement of Methyl Methacrylate by Sustainable Bio-Based Isobornyl Methacrylate in Latex Pressure Sensitive Adhesive. *Int. J. Adhes. Adhes.* **2020**, *100*, 102623.
- (21) Bohre, A.; Avasthi, K.; Novak, U.; Likozar, B. Single-Step Production of Bio-Based Methyl Methacrylate from Biomass-Derived Organic Acids Using Solid Catalyst Material for Cascade Decarboxylation–Esterification Reactions. *ACS Sustainable Chem. Eng.* **2021**, *9* (7), 2902–2911.
- (22) Oh, X. Y.; Ge, Y.; Goto, A. Synthesis of Degradable and Chemically Recyclable Polymers Using 4,4-Disubstituted Five-Membered Cyclic Ketene Hemiacetal Ester (CKHE) Monomers. *Chem. Sci.* **2021**, *12* (40), 13546–13556.
- (23) Akiya, N.; Savage, P. E. Roles of Water for Chemical Reactions in High-Temperature Water. *Chem. Rev.* **2002**, *102* (8), 2725–2750.
- (24) Weingärtner, H.; Franck, E. U. Supercritical Water as a Solvent. *Angew. Chem. Int. Ed Engl.* **2005**, *44* (18), 2672–2692.
- (25) Osada, M.; Shoji, S.; Suenaga, S.; Ogata, M. Conversion of N-Acetyl-d-Glucosamine to Nitrogen-Containing Chemicals in High-Temperature Water. *Fuel Process. Technol.* **2019**, *195*, 106154.

- (26) Osada, M.; Nishiwaki, M.; Watanabe, T. Environment-Friendly Utilization of Squid Pen with Water: Production of  $\beta$ -Chitin Nanofibers and Peptides for Lowering Blood Pressure. *Int. J. Biol. Macromol.* **2021**, *189*, 921–929.
- (27) Ishii, S.; Sezai, A.; Kohsaka, Y.; Deguchi, S.; Osada, M. High-Speed Synthesis of Thermo-Responsive Polymers by Boosted Polymerization of N,N-Diethyl Acrylamide in High-Temperature Water. *Ind. Eng. Chem. Res.* **2022**, *61* (46), 17012–17016.
- (28) Adschiri, T.; Hirose, S.; Malaluan, R.; Arai, K. Noncatalytic Conversion of Cellulose in Supercritical and Subcritical Water. *J. Chem. Eng. Jpn.* **1993**, *26* (6), 676–680.
- (29) Townsend, S. H.; Abraham, M. A.; Huppert, G. L.; Klein, M. T.; Paspek, S. C. Solvent Effects during Reactions in Supercritical Water. *Ind. Eng. Chem. Res.* **1988**, *27* (1), 143–149.
- (30) Sato, O.; Mine, E.; Osada, M.; Hiyoshi, N.; Yamaguchi, A.; Bando, K. K.; Masuda, Y.; Shirai, M. Depolymerization of Poly(Ethylene Terephthalate) to Terephthalic Acid and Ethylene Glycol in High-Temperature Liquid Water. *Chem. Lett.* **2009**, *38* (3), 268–269.
- (31) Sato, O.; Arai, K.; Shirai, M. Hydrolysis of Poly(Ethylene Terephthalate) and Poly(Ethylene 2,6-Naphthalene Dicarboxylate) Using Water at High Temperature: Effect of Proton on Low Ethylene Glycol Yield. *Catal. Today* **2006**, *111* (3), 297–301.
- (32) Inokuma, Y.; Yoneda, T.; Ide, Y.; Yoshioka, S. Aliphatic Polyketones as Classic yet New Molecular Ropes for Structural Diversity in Organic Synthesis. *Chem. Commun.* **2020**, *56* (64), 9079–9093.
- (33) Smith, M. B. Basic Cleavage of  $\beta$ -Keto Esters and  $\beta$ -diketones. In *March's Advanced Organic Chemistry*, 8th ed; John Wiley & Sons, Inc, 2020; p. 757.
- (34) Mohammad, O.; Onwudili, J. A.; Yuan, Q. A Critical Review of The Production of Hydroxyaromatic Carboxylic Acids as A Sustainable Method for Chemical Utilisation and Fixation of CO<sub>2</sub>. *RSC Sustain.* **2023**, *1* (3), 404–417.