

**Plastics to Fertilizers: Chemical Recycling of a Bio-based Polycarbonate as a Fertilizer Source**

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ARTICLE

Plastics to Fertilizers: Chemical Recycling of a Bio-based Polycarbonate as a Fertilizer Source

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Commodity polymer materials are now required to be environmentally friendly due to problems associated with resource depletion and low recycling rates, which has promoted the development of circular material systems. Herein, a novel concept is introduced, where a polymer is used as a source of a fertilizer. To demonstrate the viability of this concept, the chemical recycling of poly(isosorbide carbonate) (PIC) is presented as a model for the next generation of plastic-recycling systems. PIC, a bio-based polymer known for its excellent physical properties, undergoes a degradation reaction with aqueous ammonia. Monitoring the degradation behavior by ¹H NMR and FT-IR spectroscopy as well as gel-permeation chromatography revealed that PIC completely decomposes within 6 h at 90 °C to afford isosorbide and urea. The utility of isosorbide and urea obtained from the degradation of PIC as fertilizers was demonstrated via plant-growth experiments. The generation of fertilizers via polymer degradation in the present study is expected to lead not only to innovative chemical recycling systems to address the environmental problems associated with polymer materials, but also to provide solutions to the food-production problems associated with the growth of the global population.

1 Introduction

Over the past century, humanity has immensely benefited from the durable and versatile polymeric materials that have emerged as a result of the development of synthetic chemistry. However, synthetic polymers also contribute to many environmental problems, such as the destruction of ecosystems, pollution, and resource depletion. In particular, polymeric materials are associated with two critical environmental problems: (i) The use of large quantities of petrochemical compounds to manufacture polymer materials and (ii) the disposal of large quantities of often non-biodegradable polymer materials without recycling after use.¹ To solve problem (i), resource-saving strategies such as restrictions on plastic bags and the use of biomass to manufacture polymer materials have been implemented. To address problem (ii), recycling of polymer materials, including reuse via reprocessing (mechanical

recycling), chemically decomposing and re-synthesis (chemical recycling), as well as the use of polymer materials as an energy source (thermal recycling) have been introduced.^{2–6} Among these approaches, polymeric materials are recycled by the mechanical recycling or chemical recycling, but mechanical recycling accompanies with the deterioration of the material due to decreasing the molecular weight during the process⁷, which cannot be permanent recycling. In contrast, polymeric materials are re-synthesized in the case of chemical recycling, which is not accompanied by deterioration of the material and can be permanent recycling as long as collecting the waste plastics. Because of this reason, chemical recycling has been focused as more environmentally friendly recycling process. Among the chemical recycling approaches, the combination of using biomass as a source of plastic and recycling plastic after use represents an ideal circular system that could contribute to a sustainable material supply and decrease the environmental load. To further improve the environmental compatibility of polymer materials, it is necessary to incorporate as many circular systems as possible in this area.⁸ However, at present, only 14% of plastic waste are recycled, while another 14% are incinerated for energy recovery; the remaining 72% are discarded.⁹ As the global standard of living increases and the global population continues to grow, the demand for polymeric materials is increasing, concurrently increasing the scale of the problem of polymer recycling. On the other hand, solutions to

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1 the problem of producing sufficient food for the increasing
2 global population are also required.¹⁰ One solution to this
3 problem is promoting the growth of plant crops, i.e., the use
4 of fertilizers.

5 The Haber–Bosch process is referred to as the “bread-from-air”
6 process, as the urea and ammonium sulfate synthesized from
7 ammonia act as fertilizers that have greatly alleviated looming
8 food-supply problems. Based on investigations by Yara
9 *International*TM, even today, more than a century after the
10 discovery of the Haber–Bosch process, nitrogen-based
11 fertilizers account for >50% of the global fertilizer production,
12 i.e., most food production is promoted using nitrogen-based
13 fertilizers.^{11,12} Obtaining such fertilizers via polymer recycling
14 would represent an ideal system, not only for the recycling of
15 polymeric materials, but also for the issue of global-food
16 production.

17 In this study, a novel concept is presented, wherein a polymer
18 serves as a fertilizer source. To demonstrate the viability of this
19 concept, which could become a game changer in simultaneously
20 solving the problems of plastic recycling and food production,
21 we focused on a bio-based polycarbonate (PC). Poly(isosorbide
22 carbonate) (PIC), a bio-based PC synthesized using non-toxic
23 and biodegradable¹⁴ isosorbide (ISB) derived from glucose
24 the diol monomer,¹⁵ has attracted interest as an alternative
25 conventional petroleum-based PCs on account of its superior
26 thermal stability and transparency^{16–25}, which is actually
27 commercially available as an ISB-based copolycarbonate in
28 various fields such as the construction, automotive industries,
29 and optical material. It is well known that the carbonate linkage

obtained via the degradation of PIC as a fertilizer was tested
using plant-growth experiments. The PIC recycling process does
not require organic solvents and yields the monomeric diols and
urea, both of which are expected to act as fertilizers, i.e., all the
degradation products are circulated in the system.

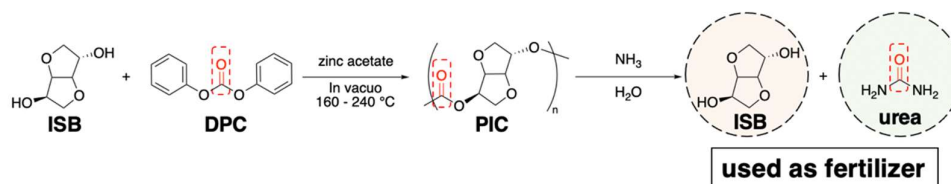
Experiments

Materials

All reagents and solvents were purchased from Tokyo Chemical Industry (Tokyo, Japan), Kanto Chemical (Tokyo, Japan), FUJIFILM Wako Pure Chemical Corporation (Tokyo, Japan), and Sigma-Aldrich (MO, USA). All reagents except for isosorbide (ISB) and diphenyl carbonate (DPC) were used without further purification. Prior to use, ISB was recrystallized from a mixture of ethyl acetate and hexane, while DPC was recrystallized from ethanol.

Measurement

¹H and ¹³C NMR spectra were recorded in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) or chloroform-*d* (CDCl₃) on a Bruker topspin AVANCE III HD500 spectrometer at 25 °C. For diffusion-ordered NMR spectroscopy (DOSY), the LED method was used (pulse program: ledbppg2s; diffusion time: 40 ms; diffusion gradient length: 2000 μs; maximum gradient strength: 51 g/cm in DMSO-*d*₆ at 25 °C).⁴² Fourier-transform infrared (FT-IR) spectra were recorded using a JEOL FT/IR-4100 spectrometer on a KBr crystal plate. As for the sample of FT-IR, characterization was conducted after a portion of suspension or solution was



Scheme 1. Synthesis of PIC via melt-polycondensation and its ammonolysis. PIC is converted into ISB and urea, which are used as fertilizers.

30 can be hydrolyzed by ammonia (ammonolysis) to give urea.^{26,27}
31 In the system we envisaged, the ammonolysis of PIC would
32 afford bio-based monomers and urea as the products once the
33 reaction proceeds completely. Although there have been many
34 reports on the degradation of polymers, most of these have
35 focused on the monomer structure and its function, as well as
36 the origin of the monomers, whether bio-based or not.^{26–37}

37 However, only few reports that focus on the use and potential
38 of the carbonyl source after polymer degradation have been
39 published.^{38–41} In the present study, we have focused on the
40 structure and utility of the degradation product from the
41 carbonyl source in the polymer repeating units as well as the
42 use of bio-based monomers (**Scheme 1**). Specifically, the
43 chemical recycling of PIC, which is expected to be a promising
44 alternative to petroleum-based plastics on account of its
45 superior properties, was conducted using ammonia treatment
46 in water. The degradation reaction and its products were
47 quantitatively characterized. The utility of the products

collected and then freeze dried. Gel-permeation chromatography (GPC) was performed at 40 °C using a JASCO HSS-1500 system with a refractive index (RI) detector. *N,N*-dimethylformamide (DMF) with lithium bromide (5 mM) were used as the eluent at a flow rate of 0.6 mL/min. Polystyrene standards (number average molecular weight (M_n): 4,430–3,242,000 g mol⁻¹; polydispersity index (PDI): 1.03–1.08) were used to calibrate the GPC system. Electro-ionization mass spectrometry (ESI-TOF-MS) measurements were carried out using a Bruker micrOTOF II.

Synthesis of PIC

PIC was synthesized using a one-pot melt-polycondensation method, in which the transesterification and polycondensation reactions were conducted in the same reactor continuously. ISB (9.63 g, 65.9 mmol), DPC (14.1 g, 65.9 mmol), and zinc acetate (6.00 mg, 31.9 μmol, 0.05 mol%) were placed in a two-necked round-bottomed

1 flask (100 mL) equipped with a mechanical stirrer. In the
2 transesterification stage, the reactants were heated to 160 °C under
3 a nitrogen atmosphere and stirred for 30 min. The temperature was
4 then gradually increased to 200 °C and maintained there for 30 min.
5 In the polycondensation stage, the temperature was gradually
6 increased to 220 °C and maintained there for 30 min under vacuum
7 (13.5 mmHg) to remove phenol. The temperature was then further
8 increased to 240 °C and maintained there for 1 h under high vacuum
9 (< 0.2 mmHg). The reaction system was then cooled to room
10 temperature under a nitrogen atmosphere. The product was
11 dissolved in chloroform, followed by precipitation into methanol.
12 After drying under vacuum, PIC was obtained as a white solid (yield
13 11.0 g, 96.7%; M_n = 14,300; PDI = 1.75).

14 Ammonolysis of PIC

15 A round-bottomed flask (50 mL) was charged with PIC (250 mg)
16 and aqueous ammonia (14.8 mol/L) to give the desired
17 stoichiometric ratio of ammonia. The reaction mixture was
18 stirred at 10–90 °C, and at reaction times of 1, 3, 6, 12, and 24 h.
19 An aliquot (2 mL) of the reaction mixture was collected and
20 freeze-dried to remove the ammonia and water. The dried
21 degradation product was used for characterization. Other
22 ammonolysis experiments were conducted in the same manner.

23 Calculation of the yield of the degradation products

24 A round-bottomed flask (50 mL) was charged with PIC (250 mg)
25 and aqueous ammonia (14.8 mol/L) to give the desired
26 stoichiometric ratio of ammonia. In the case of the reaction
27 at 90 °C, the reaction mixture was stirred, and at various reaction
28 times 1.00 mL of the reaction mixture was collected and freeze-
29 dried. Then, DMSO- d_6 (1.00 mL) and toluene (50.0 μ L; internal
30 standard) were added to the dried sample to prepare a solution
31 for ^1H NMR measurements (sample: 0.500 mL).

32 Plant growth test

33 The seeds of *Arabidopsis thaliana* ecotype Col-0 were surface
34 sterilized with bleach and sown onto medium (Table S1)
35 solidified with 1% Gellan Gum supplemented with 1% sucrose.
36 The concentration of each nutrient, except for nitrogen source,
37 was based on Fujiwara *et al.*⁴³ After incubation for two days at
38 4 °C, the plates were placed vertically and grown at 22 °C for
39 two weeks under 16h light/8 h dark condition.

41 Results and discussion

42 Synthesis of PIC

43 We synthesized PIC for the ammonolysis investigation via
44 melt-polycondensation using ISB as the diol monomer and
45 diphenyl carbonate as the carbonyl source in the presence of
46 zinc acetate, which is known to be an efficient polymerization
47 catalyst for PIC (Scheme 1).²² PIC was obtained in 96.7% yield as
48 a white solid with a number-average molecular weight (M_n) of
49 14,300 and a polydispersity index (PDI) of 1.75, which was
50 determined by GPC using DMF as the eluent. ^1H and ^{13}C NMR
51 measurements were conducted to characterize the polymeric
52 product. The signals in the ^1H NMR spectrum were in good

agreement with those of the protons in the PIC molecular chain
and its end groups (Figure S-2). The M_n calculated using ^1H NMR
(8,300) was smaller than the value obtained from GPC. This
could be due to the difference between the hydrodynamic radii
of PIC and the polystyrene standard in the DMF solution.
Furthermore, the signals in the ^{13}C NMR spectrum were also in
good agreement with the carbon atoms in PIC (Figure S-3).
Three different carbonyl-carbon signals were observed around
154 ppm, in accordance with the bonding behavior of the ISB
monomer. These results confirmed the synthesis of PIC.

Ammonolysis of PIC

The synthesized PIC was then used for ammonolysis. The
ammonolysis was conducted in water, which is a more
environmentally friendly solvent than other typical organic
solvents. For the initial investigation, we added 20 equivalents
of ammonia per repeating unit of PIC ($[\text{NH}_3]_0/[\text{PIC}]_0 = 20$) and
chose atmospheric pressure and 30 °C as the initial
ammonolysis reaction conditions in order to prevent the
thermal decomposition of urea under harsher conditions.²⁷ The
ammonolysis was conducted heterogeneously during the initial
stage of the reaction given the poor solubility of PIC in water.
The reaction mixture became gradually homogeneous and was
completely transparent after 24 h (Figure S-4). As the
ammonolysis of PIC would afford hydrophilic degradation
products such as ISB and urea, this result visually suggested that
the ammonolysis was proceeding as expected. The degradation
products were collected at different reaction times and
characterized using GPC and ^1H NMR measurements to monitor
the reaction behavior. The GPC results showed that the
molecular weight of PIC gradually decreased, and the PIC peak
completely disappeared after 24 h (Figure 1a). Similarly, in the
 ^1H NMR spectra (Figure 1b), the signals corresponding to the
methylene protons adjacent to the carbonate groups in the
polymer main chain (4.95–5.10 ppm, highlighted as gray square)
gradually decreased and completely disappeared after 24 h. In
the ^1H NMR spectrum of the degradation product after 24 h of
reaction, signals corresponding to the ISB (red letters in the ^1H
NMR spectrum after 24 h in Figure 1b) and urea (5.39 ppm)
were observed. These results strongly support the potential of
the ammonolysis of PIC to afford urea as a degradation product
under these mild reaction conditions.

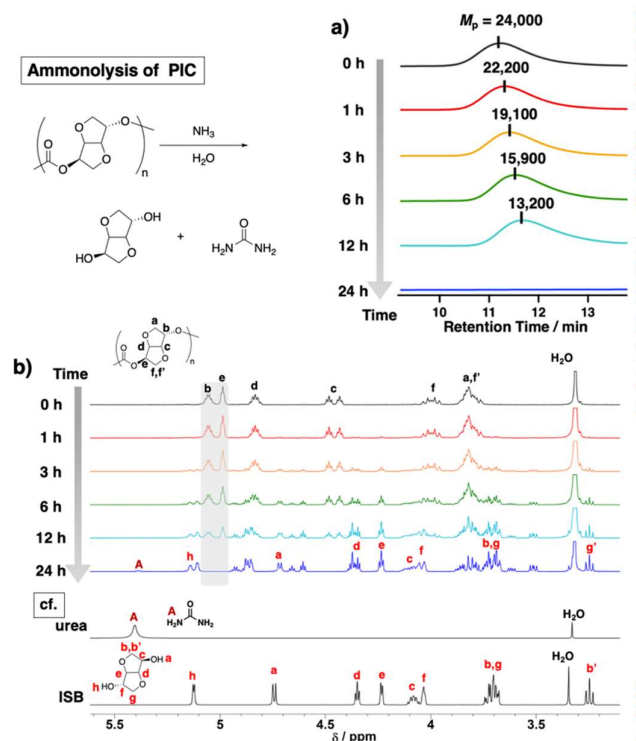


Figure 1. (a) GPC profiles of the degradation products during ammonolysis (eluent: DMF; detector: RI; polystyrene standards). (b) ^1H NMR spectra of the degradation products during the ammonolysis (500 MHz, 25 $^\circ\text{C}$, $\text{DMSO}-d_6$).

Although the presence of signals corresponding to ISB and urea was confirmed in the ^1H NMR spectrum, other signals corresponding to unassigned products were also detected (for example, the signals at 4.6–4.7, 3.8–3.9, and 3.5–3.7 ppm **Figure 1b**, highlighted as blue square). These signals were tentatively assigned to ISB derivatives with carbamate esters both hydroxyl groups of ISB, as the general ammonolysis of PC proceeds via a nucleophilic substitution of an amine at the carbonate groups.³¹ To confirm the formation of carbamate ester derivatives of ISB, isorbide dicarbamate (**ISB-DC**) was synthesized as a model compound to compare its ^1H NMR spectra with those of the degradation products. Signals for the methylene protons adjacent to the carbamate and amine protons on the carbamate groups similar to those in the **ISB-DC** spectrum were observed in the ^1H NMR spectrum of the degradation products, which suggests that **ISB-DC** is present in the degradation products (**Figure 2**). However, there were also other unassigned signals that do not correspond to **ISB-DC** (marked with an asterisk in **Figure 2**). We then conducted the ammonolysis of **ISB-DC** in the same manner as that of PIC (**Scheme S-3**) and analyzed the degradation products using NMR spectroscopy. In the resulting spectrum, signals that do not correspond to urea, ISB, or **ISB-DC** were observed at the same chemical shifts as those in the spectrum of the ammonolysis of PIC (**Figure S-5**). This result suggests that these

signals correspond to degradation products that do not contain a carbonate bond. The degradation products of PIC after 24 h were then analyzed using mass spectrometry. In the mass spectrum, in addition to the peaks corresponding to ISB ($m/z = 143.13$, $[\text{M}-\text{H}]^-$) and **ISB-DC** ($m/z = 255.06$, $[\text{M}+\text{Na}]^+$), a peak at $m/z = 212.05$ ($[\text{M}+\text{Na}]^+$) was observed (**Figure S-6, S-7**). This peak was tentatively assigned to ISB derivatives with a carbamate ester substituted on one of the hydroxy groups of ISB (isorbide mono-carbamate; **ISB-MC** in **Scheme 2**). These results indicate that the ammonolysis proceeded via the generation of ISB carbamate derivatives, i.e., **ISB-DC**, **ISB-MC**, and **ISB-MC**, as intermediates to subsequently afford urea and ISB as the final degradation products (**Scheme 2**).

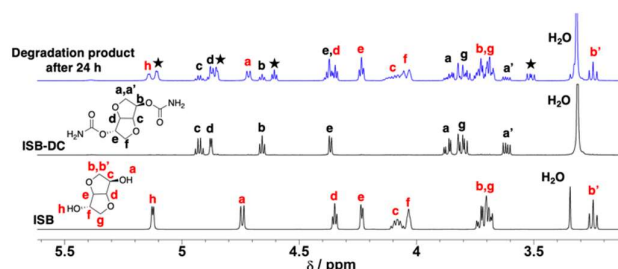
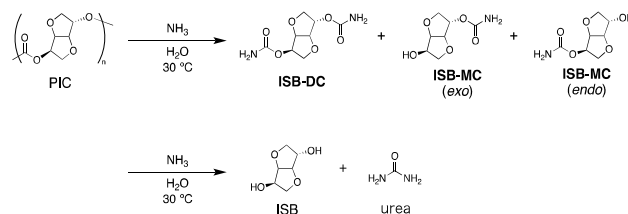


Figure 2. Comparison of the ^1H NMR spectrum of the degradation products with those of the expected products.



Scheme 2. Reaction mechanism for the ammonolysis of PIC

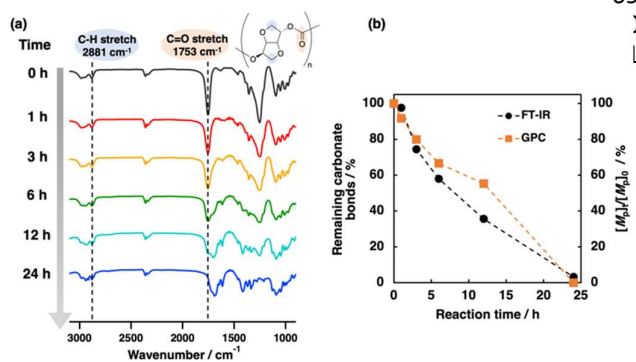
Quantitative evaluation of the ammonolysis of PIC

To further investigate the details of the ammonolysis of PIC, the degradation products were analyzed using FT-IR. **Figure 3a** shows the FT-IR spectra of the degradation products. The C=O stretching absorption peak at 1753 cm^{-1} gradually shifted to lower wavenumbers. Since the carbonyl-stretching absorption of carbamate bonds is observed at lower wavenumbers than that of carbonate bonds, this result suggests that carbamate bonds were gradually generated as the ammonolysis progressed, indicating that **ISB-DC** and **ISB-MC** are generated as intermediates during the degradation process of PIC. As the C–H stretching absorption of isorbide at 2881 cm^{-1} remained unchanged during the ammonolysis, i.e., the number of C–H bonds in the reaction system remained constant, the fraction of carbonate bonds remaining, i.e., the conversion of the carbonate bonds, can be estimated from the transmittance of the C=O stretch at 1753 cm^{-1} relative to that of the C–H stretch at 2881 cm^{-1} , which allows a quantitative evaluation of the

1 ammonolysis. The quantitative evaluation by FT-IR is more
2 convenient than ^1H NMR measurement in such heterogeneous
3 reaction condition because it is impossible to conduct the
4 reaction in the NMR sample tube and analysis the reaction
5 mixture directly.

6 A calibration curve for estimating the conversion of the
7 carbonate group based on the peak intensities in the IR spectra
8 ($D_{\text{C=O}}/D_{\text{C-H}}$) was prepared by changing the mixing ratios of PIC
9 and isosorbide (for details, see the ESI and Figure S-8).
10 Consequently, the percentage of remaining carbonate bonds
11 each reaction was calculated and plotted as a function of
12 reaction time (Figure 3b). The carbonate groups remaining
13 the PIC gradually decreased and became nearly zero after 24 h.
14 The residual polymer ratio ($[M_p]_t/[M_p]_0$), i.e., the ratio of the
15 peak top molecular weight at a given reaction time ($[M_p]_t$)
16 relative to the initial value ($[M_p]_0$), where $[M_p]_t/[M_p]_0 = 0$ would
17 indicate no polymer in the degradation product, was also
18 estimated from the GPC profiles during the reaction and
19 compared with the remaining carbonate bonds estimated using
20 the FT-IR spectra. The results showed good agreement
21 demonstrating the successful quantitative evaluation of the
22 ammonolysis.

23

24
25

26 **Figure 3.** (a) FT-IR spectra of the degradation products during
27 the ammonolysis (KBr). (b) Remaining carbonate bonds
28 estimated based on the FT-IR data (black) and remaining mass
29 ($[M_p]_t/[M_p]_0$) calculated based on GPC data (orange) during the
30 ammonolysis.

31

32 Optimization of the reaction conditions for the ammonolysis

33 Under the initial conditions used for the ammonolysis of PIC,
34 PIC was degraded to small molecules within 24 h, but
35 intermediates such as ISB-MC and ISB-DC were still present
36 addition to urea (Figure 2). Although urea was obtained under
37 these reaction conditions, complete degradation of PIC was
38 achieved, not even after 24 h. Therefore, we further
39 investigated the optimization of the degradation reaction of PIC
40 with ammonia.

41 First, we studied the effect of the initial ammonia
42 concentration ($[\text{NH}_3]_0/[\text{PIC}]_0 = 0$ to 50) on the ammonolysis
43 of PIC without changing the reaction temperature (30 °C). The
44 degradation products obtained from the ammonolysis were
45 analyzed using both FT-IR and GPC (Figures S-9 and S-10), and
46 both the residual polymer ratio ($[M_p]_t/[M_p]_0$) and remaining

carbonate bonds during the ammonolysis were plotted as a
function of the reaction time (Figure 4a and 4b). Both sets of
results show that, except for the case of $[\text{NH}_3]_0/[\text{PIC}]_0 = 0$, where
PIC was not degraded, the degradation of PIC to small molecules
depends on the initial ammonia concentration. For $[\text{NH}_3]_0/[\text{PIC}]_0$
 ≥ 30 , the degradation was complete after 12 h; this degradation
is faster than at $[\text{NH}_3]_0/[\text{PIC}]_0 = 20$. Conversely, at $[\text{NH}_3]_0/[\text{PIC}]_0$
 $= 10$, complete degradation to small molecules was not
achieved, not even after 24 h. These results show that the
degradation is accelerated with increasing initial ammonia
concentration. However, the degree of acceleration between
30 eq. and 50 eq. was not as high as that between 10 eq. and 30
eq., which implies that the acceleration of the ammonolysis
with increasing initial ammonia concentration reaches a
threshold where ammonia is saturated relative to the PIC solid
interface, i.e., a reaction-rate-determining state predominates
for $[\text{NH}_3]_0/[\text{PIC}]_0 > 30$. Therefore, the ammonolysis proceeded
most efficiently when 30 eq. of ammonia was applied. Based on
this result, we calculated the ISB yield using ^1H NMR (reaction
conditions: 30 °C; $[\text{NH}_3]_0/[\text{PIC}]_0 = 30$; Figure S-13). The resulting
ISB yield after 24 h was only 45.3%. This result implies that
although the degradation of PIC was accelerated by adjusting
the initial ammonia concentration, the degradation was still
incomplete after 24 h.

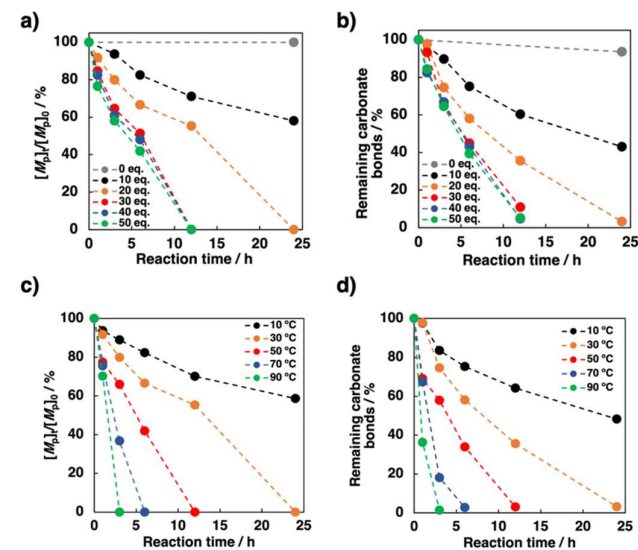


Figure 4. a) $[M_p]_t/[M_p]_0$ (residual polymer ratio) and b)
carbonate bonds remaining in the degradation products during
ammonolysis using different ammonia concentration
conditions. c) $[M_p]_t/[M_p]_0$ (residual polymer ratio) and d)
carbonate bonds remaining in the degradation products during
ammonolysis using different reaction temperatures.

The low yield of ISB was attributed to the low reactivity of
ammonia toward the carbonate bonds at 30 °C. Thus, we
subsequently investigated the dependence of the yield on the
reaction temperature. The degradation products obtained at
various reaction temperatures were analyzed using FT-IR and

1 GPC (Figures S-11 and S-12), and the results are plotted 57
 2 Figure 4c and 4d as the residual polymer ratio $[M_p]_t/[M_p]_0$ and
 3 remaining carbonate bonds during the ammonolysis. The rate
 4 of the degradation reaction increased in proportion to the
 5 temperature. When the reaction was conducted at 90 °C, the
 6 PIC was completely degraded to the corresponding small
 7 molecules within 3 h, which is much faster than when the
 8 reaction is carried out at 30 °C (24 h). The ISB yield in the
 9 ammonolysis with reaction conditions of 90 °C and $[\text{NH}_3]_0/[\text{PIC}]_0$
 10 = 30 was monitored using ^1H NMR spectroscopy, which revealed
 11 that the concentration of ISB increased with increasing reaction
 12 time to afford ISB in 97.4% yield after 6 h (Figure S-14). The urea
 13 yield was calculated in a similar manner (for details, see the ESI).
 14 After 6 h, urea was generated in 69.4% yield, which is lower than
 15 the yield of ISB. It seems that the hydrolysis reaction also
 16 occurred as a side-reaction in the aqueous ammonia solution
 17 and resulted in a small amount of the carbonyl source in the
 18 polymer being converted into CO_2 instead of urea (Scheme S-4).
 19 The ^1H DOSY NMR spectrum revealed that the degradation
 20 product is a mixture of urea and ISB without any other
 21 compounds, i.e., ISB-MC and ISB-DC were not present after
 22 (Figure S-16). Thus, complete degradation to the targeted
 23 degradation products was achieved by simply increasing the
 24 reaction temperature. Furthermore, the reaction proceeded
 25 without any catalyst, demonstrating that the ammonolysis
 26 PIC can be easily performed using aqueous ammonia and
 27 heating. Thus, the ammonolysis of PIC is operationally simple
 28 and environmentally friendly from the viewpoint of chemical
 29 recycling. From the viewpoints of sustainability, reuse of excess
 30 ammonia after the reaction was evaluated. Specifically, first
 31 ammonolysis reaction was conducted in the same manner
 32 the optimized condition and then further PIC was added into
 33 the reactor. Consequently, second shot PIC was completely
 34 degraded to ISB and urea within 6 h (Figure S17). The titration
 35 measurement of the residual ammonia after second
 36 ammonolysis experiment was performed to show the effective
 37 use of ammonia in this study. The ammonia in reactor remained
 38 almost theoretically (Figure S 18), demonstrating that the
 39 residual ammonia can be used for further ammonolysis
 40 experiment.

41 Plant growth using the PIC-degradation products

42 Finally, a plant-growth test was conducted using the
 43 degradation products obtained from the ammonolysis of PIC.
 44 Urea, which is a component of the degradation products, is a
 45 well-known fertilizer used worldwide to promote plant growth,
 46 on the other hand, ISB is not used as a fertilizer. However, ISB
 47 a non-toxic and sugar-based compound, so it would not be
 48 expected to exert a negative impact on plant growth. Given that
 49 the degradation products contained only urea and ISB, they
 50 could be used directly as a fertilizer without purification. The
 51 purpose of the plant-growth test was to demonstrate whether
 52 the degradation products from PIC have a negative impact on
 53 plant growth or not.

Table 1. Fertilizers used in the plant growth experiment

| Entry | 300 mM urea | 300 mM urea & ISB | 300 mM degradation product | Water with other minerals | Total volume |
|-------|-------------|-------------------|----------------------------|---------------------------|--------------|
| 1 | 2.5 mL | 0 mL | 0 mL | 247.5 mL | 250 mL |
| 2 | 0 mL | 2.5 mL | 0 mL | 247.5 mL | 250 mL |
| 3 | 0 mL | 0 mL | 2.5 mL | 247.5 mL | 250 mL |

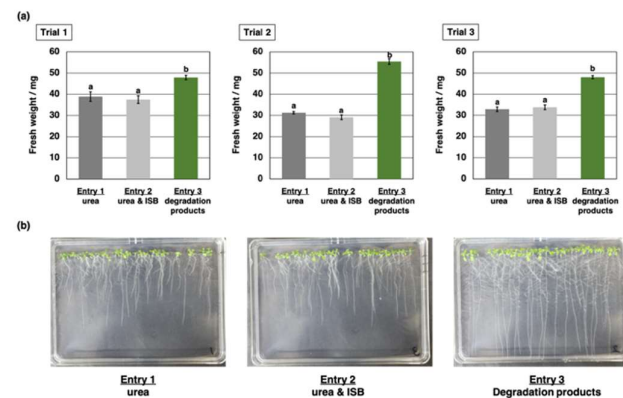


Figure 5. a) Fresh weight of *Arabidopsis thaliana*. Values represent mean values \pm standard deviation ($n = 10$). Different letters indicate significant differences (Tukey's HSD, $p < 0.05$), and b) photographs of the *Arabidopsis thaliana* in each plant-growth test.

Arabidopsis thaliana, which was used as model plant, was grown for 2 weeks (for details, see the ESI). Three aqueous solutions, i.e., a solution of commercially available urea (Entry 1), a solution of commercially available urea and ISB (Entry 2), and a solution of the degradation products from PIC (conditions: 90 °C and $[\text{NH}_3]_0/[\text{PIC}]_0 = 30$; Entry 3), were prepared as shown in Table 1 (for details, see Table S2) and applied in the plant-growth test using *A. thaliana*. The fresh weights and photographs of *A. thaliana* after 2 weeks using the different solutions are presented in Figure 5. *A. thaliana* grew well in all the solutions, demonstrating that the degradation products from PIC did not have any negative impact on plant growth. *A. thaliana* exhibited more growth than in the control experiment with only urea (Entry 1), indicating that ISB has a positive rather than a negative impact on the plant growth. To further investigate the effect of ISB as fertilizer, only ISB was added to the plant. Consequently, when only ISB was added, the effect as a fertilizer was not observed (Trial 4, Figure 19, Table S2 entry 4-6). However, when ISB was added combining with urea, which is same condition as degradation products, the fertilizer effect was better than the case of adding only urea. This result implied that ISB has the promotion effect for plant growth of *A. thaliana* in the presence of urea. Although investigations into the plant growth using urea and ISB remain ongoing, e.g., uptake of the degradation products by the plants, the present results are sufficient to serve as proof-of-concept for our hypothesis, i.e., that the degradation products from PIC can successfully be used as fertilizers without purification. This chemical recycling of a polycarbonate using ammonia is operationally simple and

- 1 environmentally friendly and thus represents an innovative 50 4
 2 ‘fertilizer-from-plastics’ system. 51
 3 52 5
 4 **Conclusions** 53
 5 We have demonstrated a novel concept based on using plastics 54 6
 6 as a source of fertilizers to address global environmental and 55
 7 food-supply issues via the chemical recycling of poly(isosorbide 56 7
 8 carbonate) (PIC), a bio-based polycarbonate that functions as a 57
 9 model for next-generation plastics. The chemical recycling 58
 10 method for PIC, which has carbonate bonds in its repeating 59
 11 units, used ammonia as a reagent to afford urea as a 60
 12 degradation product. The optimal reaction conditions were 61
 13 found to be 90 °C and $[\text{NH}_3]_0/[\text{PIC}]_0 = 30$. The complete 62
 14 degradation of PIC to afford only ISB and urea via simple heating 63
 15 in the environmentally friendly solvent water was achieved in 64
 16 the absence of any catalyst. Furthermore, we examined the use 65
 17 of the degradation products as a fertilizer, which revealed that 66
 18 the untreated degradation products could be used without any 67
 19 problems. Ammonia is one of the most widely produced 68
 20 chemicals in the world, and many researchers have been 69
 21 actively developing increasingly effective methods to produce 70
 22 NH_3 , which will make the production of ammonia simpler and 71
 23 more affordable.⁴⁴ Therefore, this method of chemical polymer 72
 24 recycling is revolutionary in terms of the usefulness of the 73
 25 degradation products of the plastics and the convenience of the 74
 26 reaction. Various types of bio-based polycarbonates have been 75
 27 reported so far,^{45–53} and their degradation products might also 76
 28 be effective fertilizers. We are convinced that the present study 77
 29 represents a milestone toward developing sustainable and 78
 30 recyclable polymer materials in the near future. The era of 79
 31 “bread from plastics” is just around the corner. 80
 32 81
- 33 **Conflicts of interest** 82
 34 There are no conflicts to declare. 83
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 41 measurements. 90
 42 91
- 43 **Notes and references** 92
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